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Nickel in tektites by activation analysis*

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(*Received* 27 *February* 1960)

Abstract—The nickel abundances of most of the major occurrences of tektites, as well as several meteorite impact glasses and obsidians, have been determined using neutron activation analysis. Iron abundances have been determined in the same specimens and Ni/Fe abundance ratios tabulated. These ratios, determined for the first time on the Libyan Desert glass, the Ivory Coast tektites, and the bediasites, indicate all these specimens fall within the known range of this ratio for the other tektite occurrences. On the basis of this ratio, major differences are observed among specimens from the indochinite tektite occurrence, but no significant differences are observed among specimens from three separate philippinite sites. The differences in the Ni/Fe ratios for tektites and known meteorite impact glasses suggest different modes of formation.

Introduction

One frequently-suggested origin of tektites is that they are products of the collisions of large meteoritic bodies with the earth or the earth's moon. Krinov (1958) has again reviewed the similarities between tektites and known examples of meteorite impact glass. He suggests that tektites are the most stable portions of such impact glasses, being preserved long after the disappearance of the original meteoritic crater.

It was postulated by Spencer (1933) that the glass formed by meteorite impact usually contains nickel, derived from the meteorite itself. This proposal was supported by the discovery of small iron–nickel spheres in specimens of silica glass from the meteorite craters at Wabar, Arabia. In the same paper Spencer also states these metallic spheres are abundant in some specimens of Darwin glass from Tasmania, although no meteoritic crater can be recognized in that locality at present.

Since the time of this suggested relation between glasses with high nickel content and meteorite-impact glasses, traces of nickel have been searched for in various types of natural glasses, including the tektites.

In most of the early analyses of tektites the analytical methods used for nickel were not of sufficient sensitivity to define the levels of the nickel abundance. Of the eleven nickel analyses in tektites summarized by Barnes (1940), nickel was reported as absent in six specimens, present as a trace in three specimens, and 235 and 470 p.p.m. in two australite specimens.

Some of the best analyses available for nickel in tektites are those of Preuss (1935) and Heide (1938a, 1938b, 1939). These investigators used an emission spectrograph to measure iron–nickel abundance ratios in tektites and related glasses. While this method was much more sensitive than the wet chemical methods previously used, the lower limit of nickel sensitivity for the technique was still approximately 8 p.p.m. Also, the method was subject to fairly high

* This work has been supported in part by the United States Atomic Energy Commission. Portions of this paper were presented at the 137th National meeting of the American Chemical Society, Cleveland, Ohio, 14 April 1960.

uncertainties for the nickel abundances near this limit. Buddhue (1946) compiled the existing data and some original analyses and reported the average nickel abundance in tektites to be 31 p.p.m.

In order to study further the possible relation of tektites to meteorite impact glasses, Barnes (1958) suggests the desirability of having many times the number of nickel analyses now available. The great sensitivity of neutron activation analysis for the determination of certain elemental abundances has been demonstrated in many papers over the last several years. In this work the nickel abundances in tektites from a representative collection of the world's occurrences are determined using the neutron activation technique. This method, as applied here, has a lower limit of sensitivity of approximately 0·5 p.p.m. of Ni. Iron analyses have also been done, using conventional chemical techniques and the Ni/Fe ratios for the specimens have been tabulated.

Experimental

Materials

All specimens, not otherwise credited, were furnished by Dr. T. P. Kohman, Carnegie Institute of Technology, Pittsburgh, Pennsylvania. To all who assisted in furnishing material for these analyses the writer is deeply appreciative.

Australite. The sample analysed is from a composite of australite fragments from the Kalgoorlie region of Western Australia. (From Dr. H. M. Hale, Director of the South Australian Museum, Adelaide, South Australia.)

Bediasite. The sample analysed, probably from Fayette County, Texas, is a fragment of a specimen obtained by Dr. Kohman from A. C. Buscha, Giddings, Texas.

Indochinites. The "Tan Hai" specimen is from Tan Hai Island just east of the Luichow Peninsula of China. This is in the northernmost part of the indochinite area. The Cambodian specimen is described only as from northern Cambodia. This is in the southern part of the indochinite area, about 550 miles south-southwest of Tan Hai. The "Dalat, Annam" specimen is from Dalat in south Viet Nam, and represents the southernmost of these three indochinites.

Indonesian tektite. The only specimen analysed was from the Sangiran Dome area near Solo, Central Java. (From Dr. G. H. R. von Koenigswald, University of Utrecht, Netherland.)

Ivory Coast tektite. A specimen described only as from the Ivory Coast of Western Africa.

Libyan Desert glass. One specimen collected by L. J. Spencer, south-western Egypt. (From Dr. M. H. Hey, British Museum (Natural History), London).

Moldavite. One specimen from Dr. T. P. Kohman, probably a Bohemian variety. It was obtained by Dr. E. F. Kohman from the widow of Herr A. Berger of Mödling bei Wien, Austria.

Philippinites. The Philippine specimens are from three prolific sites on Luzon Island. (All specimens are from Dr. H. Otley Beyer, Director, Museum and Institute of Archaeology and Ethnology, Manila, Philippines.) These sites, each furnishing tektites of distinctive appearance, are the "Anda" site, Pangasinan Province, "Pugad Babuy" site, Bulakan Province, and "Santa Mesa" site, Rizal Province.

Thailand tektite. The only specimen analysed from Thailand is from near the village of Nan Kung, Province of Sakon Nakhon. This locality, near the border of Laos, is in the central part of the indochinite area.

Aouelloul glass. An impact glass from Aouelloul crater, Adrar, western Sahara, Africa.

Darwin glass. A glass of possible impact origin from the vicinity of Ten Mile Hill near Queenstown on the west coast of Tasmania. (From Dr. S. W. Carey, University of Tasmania, Hobart, Australia.)

Americanite. An obsidian sample of unusual character from near Macusani, Peru. (From Dr. V. E. Barnes, Bureau of Economic Geology, The University of Texas, who received it from Dr. R. Martin, Shell Oil Company, Calgary.)

Apache Tears. A form of obsidian; reportedly from Arizona. (Several specimens were purchased from a mineral dealer.)

Chemistry

Approximately 0·3 g interior samples of the tektites were powdered in a vibration ball mill and irradiated in the "rabbit" of the Argonne CP-5 reactor at a flux density of 10^{13} neutrons cm^{-2} sec^{-1} for a period of 1 hr. The sample was allowed to "cool" for 1 to 2 hr after removal from the reactor before starting the chemical separations.

The powdered sample was then fused with Na_2CO_3 in a platinum crucible, and a known amount of nickel nitrate carrier was added to allow determination of the chemical yield. The fusion cake was dissolved in concentrated HCl and transferred to a beaker. Concentrated HNO_3 was added and the solution warmed to assure solution of any fine metallic particles.

The resulting clear solution was diluted with distilled water and $Fe(OH)_3$ precipitated by addition of NH_4OH. The supernatent obtained after centrifugation was separated and made just acid with acetic acid. Nickel was precipitated by addition of an alcohol solution of dimethylglyoxime. This precipitate of nickel dimethylglyoxime was separated by centrifugation, dissolved in HNO_3, diluted with distilled water, scavenged with CuS and reprecipitated at pH 6·5 with additional dimethylglyoxime solution. This final precipitate was filtered on a weighed filter paper, dried, weighed and mounted for counting. The average chemical yield for nickel was 70 per cent with the lowest being equal to 62 per cent.

Iron analyses as reported here were done by conventional gravimetric techniques on separate 0·3–0·5 g samples taken from the same batch used for the respective nickel analysis. The samples for iron analysis were dissolved in $HF–H_2SO_4$, treated with HCl, aqua regia, and were finally made up to a 9 M HCl solution. Several drops of $KMnO_4$ were added to assure oxidation of Fe^{2+} to Fe^{3+}. This solution was extracted with successive equal volumes of *iso*propyl ether. The iron in the ether phase was back-extracted with distilled water, precipitated with NH_4OH, filtered, and ignited to Fe_2O_3. Duplicate analyses were done for most specimens. The technique was determined to be quantitative by checks with standard samples.

Flux monitors

The absolute amount of nickel in the specimen was determined by comparison of the counting rate of the sample nickel separated as above and corrected for chemical yield with the counting rate of a known amount of nickel nitrate (the flux monitor) irradiated simultaneously in the same irradiation package. The nickel nitrate aliquot of a standard solution was evaporated on high-purity aluminium foil disks for the irradiation in the manner used previously in this laboratory (Ehmann and Huizenga, 1959). After irradiation these foils were rinsed repeatedly with concentrated HNO_3 to remove the evaporated nickel nitrate. A known amount of nickel nitrate carrier was added for chemical yield determination and nickel dimethylglyoxime precipitated for counting, as above. Flux monitor chemical yields were 95 to 100 per cent.

Counting

Counting was usually started 3–4 hr after the sample had been removed from the pile. Nickel was determined by counting the 1·5 MeV γ-ray emitted by 2·56 hr half-life Ni^{65}. The radionuclide Ni^{65} was formed in the pile by a (n,γ) reaction on stable Ni^{64} (1·16 per cent natural isotopic abundance, $\sigma = 1{\cdot}6$b).

The counting was done with a 3 in $\times$ 3 in. NaI crystal (37 per cent geometry) scintillation detector coupled to a 200-channel pulse–height analyser. The Ni^{65} γ-ray photo-peak was identified both by energy calibration and half-life. This γ-counting technique has the advantage over β-counting techniques previously used for nickel determinations of requiring less radio-chemical decontamination, due to the ease of energy discrimination using pulse–height analysis. In the usual case an integrated counting rate of between 10^3 and 10^4 counts per 20 min was recorded above background in the 1·5 MeV γ-ray photo-peak. Statistical errors due to counting are, therefore, of the order of from 1 to 3 per cent. In the case of the Libyan Desert glass fewer counts were recorded, and this error is of the order of 5 per cent. In each case additional 20 min counts were taken at intervals of several hours to follow the 2·56 hr half-life decay of Ni^{65}.

Results

The results of this work together with a compilation of some of the best previous analyses are given in Table 1. Reference to this table provides a rather complete

picture of nickel abundances and Ni/Fe ratios for the major tektite occurrences. Notable omissions are specimens from the recently established Georgia occurrence (Barnes and Bruce, 1959; Cohen, 1959) and specimens from the Malayan peninsula. It is hoped specimens of these occurrences may become available for analysis in the future.

The place name listed under the "Sample" column refers to the specimen used in this work, where a value is given. The data from previous work are given for the same regions according to the best estimates of location from the descriptions given. No specific site was listed for the philippinite analysed by Heide (1938a), but it was most probably from the area of the Santa Mesa site.

The result for the americanite specimen is listed as a rather high upper limit, due to an unexpected high background in the area of the Ni^{65} photo-peak. This background appeared to be due to a rather high impurity level of Cu^{64} with a γ-ray energy of 1·34 MeV. This was observed in no other sample. Nickel was definitely observed in the specimen of Apache Tears. However, with the irradiation times and sample sizes used in this work, the possible error in the integrated counting rate at this low level near the limit of sensitivity is significant, and the result is reported as $\leq 0{\cdot}5$ p.p.m. As previously stated, the statistical errors due to counting for the remainder of the specimens range from approximately 1 to 5 per cent.

The Ni/Fe ratios in Table 1 are reported in units of Ni/Fe $\times 10^4$. Using this unit, the range of this ratio for the specimens of interest is from approximately 1·0 for obsidians to 1000 for siderites.

Discussion

It is seen from the data of Table 1 that even with this larger sample of tektite occurrences, the Ni/Fe ratio for tektites in no case reaches even the lowest value of this ratio reported for the known meteorite impact glasses. In fact, most of the tektites have Ni/Fe ratios from ten to twenty times lower than the known meteorite impact glasses.

Reference to a list of the world's meteorite craters (Prior and Hey, 1953) indicates that most, if not all known meteorite craters where silica glass has been found, were probably formed by siderites. This is demonstrated by the discovery of siderite fragments near, or actually in many of these craters. No large craters are known that can be definitely ascribed to the collision of a very large stony body with the earth, although such collisions may have occurred. It might be expected that such craters would differ in their physical characteristics from those formed by large iron–nickel bodies, and, in fact, be more difficult to detect.

If an impact origin for tektites is to be considered, the low Ni/Fe ratios for tektites are more consistant with impacts by objects having a lower nickel content than siderites. Impacts by large stony bodies, or a collision of the head of a comet with the earth (Urey, 1957) would appear to be more likely.

The comparison of the Ni/Fe ratios for tektites with those for obsidians shows a relatively higher nickel content in tektites. The differences are not so great, however, as for the comparison of the meteorite impact glasses with tektites. It would be desirable to determine this ratio in a larger and more representative collection of obsidians. The overall Ni/Fe ratio for igneous rocks listed by

Table 1.

Sample	Previous work				This paper		
	Ref.	Ni (p.p.m.)	Fe (p.p.m. × 10^{-3})	Ni/Fe (× 10^4)	Ni (p.p.m.)	Fe (p.p.m. × 10^{-3})	Ni/Fe (× 10^4)
Tektites							
australite (Western Australia)	*	28	37	7·6	20	32	6·2
bediasite (Fayette Co., Texas)	—	—	—	—	14	24	5·8
indochinites							
(Tan Hai, Hainan)	*	28	40	7·0	9·8	32	3·1
(Northern Cambodia)	*	200	40	50	126	37	34
(Dalat, Annam)	*	150	36	42	129	38	34
Indonesian tektites							
(Billiton Borneo)	*	275	44	63	—	—	—
(Central Java)	†	200	40	50	216	38	57
Ivory Coast tektites (Western Africa)	—	—	—	—	105	47	22
Libyan Desert glass (Egypt)	*	<8 (n.d.)	2·3	—	3·3	3·3	10·0
moldavite (Bohemia)	*	16	19	8·4	9·2	9·2	10·0
philippinites							
(Anda Site)	—	—	—	—	32	39	8·2
(Pugad Babuy Site)	—	—	—	—	22	39	5·6
(Santa Mesa Site)	‡	31	39	8·0	26	34	7·6
Thailand tektites							
(Western-Bo Ploi)	§	47	37	13	—	—	—
(Eastern-Nan Kung)	—	—	—	—	14	30	4·7
Impact Glasses							
Aouelloul glass (Africa)	**	170	22	77	260	14	190
Darwin glass (Tasmania)	*	310	18	170	162	16	100
Henbury glass (Australia)	*	940	47	200	—	—	—
Wabar glass (Arabia)	*	860	35	250	—	—	—
Obsidians							
americanite (Peru)	*	<8 (n.d.)	—	—	<5 (n.d.)	3·6	—
Apache Tears (Ariz.)	—	—	—	—	≤0·5	4·1	≤1·2
Meteorites							
achondrites (chondritic)	††	—	—	140	—	—	—
chondrites	††	—	—	540	—	—	—
siderites	††	—	—	945	—	—	—

n.d. = not detected.

* Preuss (1935).
† Heide (1939).
‡ Heide (1938a).
§ Heide (1938b)
** Smith and Hey (1952).
†† MacDonald (1959).

Rankama and Sahama (1950) is 16 $\times$ 10^{-4}. This is within the range found for the tektites.

Several interesting features are noted for individual tektites. The Ni/Fe ratio of Libyan Desert glass is nearly the same as for a number of other tektite occurrences and is identical to that for the moldavite specimen. The Libyan Desert glass has often been excluded from the tektites and has been compared to meteorite impact glasses. The low Ni/Fe ratio suggests that the Libyan Desert glass must be considered together with the other tektite occurrences in work bearing on the origin of tektites.

The Ni/Fe ratio for the Ivory Coast tektite indicates that this is, indeed, a separate tektite occurrence. The ratio for this specimen occupies a place mid-way between the southern indochinites and the Indonesian tektites with their high nickel abundances, and the remaining occurrences with their relatively-low nickel abundances. It is seen, therefore, that we may no longer divide the tektite occurrences into two simple groups on the basis of their nickel content, as was suggested by Preuss (1935). Instead, there would appear to be examples of tektites having Ni/Fe ratios over the entire range from approximately 3·1 to 63.

It is of interest to note that the indochinite occurrence has produced specimens with both the lowest and among the highest Ni/Fe ratios determined. These specimens appear to be at one extreme of the known range, or at the other, with no truly intermediate specimens recorded to date. This is strong evidence that the indochinites represent at least two separate occurrences, as was also noted by Preuss (1935). On the other hand, these data indicate no significant differences in the Ni/Fe ratio for the three philippinite sites, in spite of quite distinct differences in physical appearance, as reported by Beyer (1955). On the basis of this data alone, no evidence is found that these different philippinite sites might represent separate occurrences.

The nickel abundance for the Texas tektites, or bediasites, is reported for the first time in Table 1. It is seen that on the basis of the Ni/Fe ratio, bediasites are most similar to the australites and the philippinites. On the basis of their physical appearances and apparent geological ages, however, these groups are probably entirely separate occurrences.

The low-nickel contents and Ni/Fe ratios found for tektites do not entirely eliminate the possibility of their formation by meteorite impact. However, on the basis of comparison to known impact glasses, their formation by siderite impacts, either terrestrial or extraterrestrial, appears to be unlikely. If it were possible to obtain a series of samples from evenly distributed locations throughout the entire area of a given tektite occurrence, the presence of a systematic variation of the Ni/Fe ratio, or the absence of such a variation, would be quite significant in finally evaluating the possibility of an origin by meteoritic impact.

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Temperatures and mass losses in iron meteorites during ablation in the earth's atmosphere

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Abstract—The results of thermomagnetic analyses of two nickel-rich ataxites (Tawallah Valley and Wedderburn) have been used to estimate the temperature gradients within their thermal alteration rims which formed during flight through the earth's atmosphere. Knowing these temperature gradients it is possible to calculate temperature rises within iron meteorites during ablation as well as the average rate of ablation of the surfaces of these meteorites (i.e. about 0·18 cm/sec). If the time during which ablation takes place averages 3·3 sec, then the average thickness of material ablated from the surfaces of these iron meteorites is about 0·6 cm. These data indicate that about 27 per cent of the pre-atmospheric mass of the Tawallah Valley ataxite and about 60 per cent of the smaller Wedderburn ataxite has been ablated in the atmosphere.

Introduction

The process of ablation plays an important part in the modification of certain pre-atmospheric properties of meteorites and may cause temperature rises within meteorites and certainly causes considerable mass losses from the surfaces of meteorites. From several points of view it is important that quantitative estimates of both temperature rises and mass losses during ablation be made. For example before it can be concluded that the natural magnetic moments measured in stony meteorites (Lovering, 1959; Stacey and Lovering, 1959) are of extra-terrestrial origin, it must be established that the interiors of the meteorites have not been heated above about 200°C while situated in the earth's magnetic field. Then again since the observed mass abundances of the various types of meteorites seen to fall on the earth's surface are commonly used to estimate their relative mass abundances in models of parent meteorite bodies, it is important that the effects of ablation in reducing the masses of meteorites observed to fall be fully understood. Actually the total mass lost by a meteorite during its flight through the earth's atmosphere is a function of the amount of material removed by ablation of the molten surface together with other losses due to mechanical crumbling and fragmentation. For the weaker stony meteorites mechanical crumbling and fragmentation may well be the major factors in determining the total mass dispersed during flight through the atmosphere. On the other hand the mechanically stronger iron meteorites probably lose most material by melting ablation.

In this paper it will be shown that measurements of the thermal gradients which existed beneath the fused crusts of meteorites during atmospheric ablation may be used to calculate temperature rises within meteorites and also the rate of ablation of their surfaces. It is difficult to find any direct method for estimating the temperature gradient beneath the fused crusts of stony meteorites during

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ablation, however, it will be shown that a study of the thermal alteration rims found on many iron meteorites can indicate temperature gradients beneath the crust during ablation. Consequently only iron meteorites have been studied in the present work but because iron meteorites have higher conductivities than stony meteorites, then temperature rises calculated within iron meteorites will form upper limits to those within stony meteorites. For the same reason ablation rates calculated for iron meteorites will tend to form upper bounds for those in stony meteorites although of course no calculations can be made at present on the masses lost by the mechanical crumbling of the stony meteorites.

Thermal alteration rims are known to occur beneath the fused crusts of iron meteorites from all the major structure classes such as the hexahedrites, octahedrites and ataxites but for most types it is difficult to make a quantitative estimate of the thermal gradients existing in these alteration rims. However, during the course of a thermomagnetic study of the composition of the magnetic phases in nickel-rich ataxites (Lovering and Parry, 1960) it was found that the α_2-phase nickel–iron alloy, which forms the dark-etching matrix in these meteorites, was very unstable during heating and the temperature at which transformation began could be accurately determined. Since the inner boundaries of the thermal alteration rims in nickel-rich ataxites mark the depths at which this transformation has begun to take place, then the temperature gradients within the alteration rims can be quantitatively estimated. It is important, then, that the thermal alteration rims in nickel-rich ataxites be more fully understood and two Australian ataxites which have well-developed rims (i.e. Tawallah Valley and Wedderburn irons) were selected for further study.

Tawallah Valley and Wedderburn Nickel-rich Ataxites

Thermal alteration rims

The microstructures of the thermally-unaltered interiors of nickel-rich ataxites have been discussed by Uhlig (1954). Both the Tawallah Valley and Wedderburn irons have microstructures which are generally typical of the nickel-rich ataxites.

The microstructure of the interior of the Tawallah Valley ataxite (Fig. 2) is composed of relatively coarse α-phase bodies oriented in a regular pattern and each one generally containing a schreibersite grain as a nucleus. Around each α-phase body there is a taenite (γ-phase nickel–iron alloy) zone which gradually merges into the dark-etching matrix material which is characteristic of nickel-rich ataxites. This matrix phase has been identified by Uhlig (1954) as metastable α_2-phase alloy which formed in these meteorites during the disruption of the metal core of the parent meteorite body. The microstructure of the interior of the Wedderburn ataxite is generally similar to that of the Tawallah Valley ataxite.

The thermal alteration rim in the Tawallah Valley ataxite varies in thickness from less than 1 mm to about 4 mm, with an average thickness of about 2·5 mm (see Fig. 1). The microstructure within the alteration rim (Fig. 3) shows that the coarse α-phase bodies remain virtually unaltered right up to the fused crust on the meteorite. However, the dark-etching matrix becomes increasingly lighter and harder to distinguish from the γ-phase alloy surrounding the coarse α-phase bodies

as the fusion crust is approached. Immediately below the fused crust the coarse α-phase bodies occur in a virtually clear matrix of what was probably γ-phase alloy. The microstructure shows that the presence of the alteration rim is due to the decomposition of the metastable α_2-phase in the matrix of the ataxite during heating in the earth's atmosphere. The inner boundary of the thermal alteration zone marks the region in which the decomposition of α_2-phase alloy is commencing while the outer boundary just beneath the fusion crust shows that decomposition and transformation of the matrix to an apparently homogeneous γ-phase alloy is virtually complete.

The Wedderburn ataxite is relatively small with a maximum diameter of 5 cm so it is not surprising that the thermal alteration rim is approximately constant in thickness, varying only from 2 to 3 mm. The microstructure of the alteration rim is generally similar to that in the Tawallah Valley ataxite.

Thermomagnetic analysis

The technique of thermomagnetic analysis can be shown to be an important tool for the identification of the magnetic phases in meteorites (Lovering and Parry, 1960). The method is particularly applicable to the determination of the nickel contents of the coexisting iron–nickel alloys in the iron meteorites and can provide important data on the thermal histories of the iron meteorites.

Briefly, thermomagnetic analysis involves measuring the force on a representative sample of a meteorite placed in an inhomogeneous magnetic field as a function of temperature (Hoselitz, 1952). If the magnetic field is high, this force is proportional to the saturation magnetic moment of the sample and it is convenient to plot the ratio of the magnetic moment of the sample at T°C to the moment at 20°C ($\sigma_T/\sigma_{20°}$) as a function of the temperature T°C. A simple single-phase system generally gives a characteristic thermomagnetic curve and the temperature at which the ferromagnetic properties vanish identifies the phase. Multiphase systems generally show a number of discontinuities representing the temperatures at which the ferromagnetic moments vanish for each phase. In this way the various constituent phases may be identified.

The α-phase nickel–iron alloys in iron meteorites are usually irreversible alloys and on heating transform rapidly to γ-phase at a characteristic temperature at which the γ-phase is non-magnetic. On cooling, the γ to α transition occurs at a lower temperature (Peschard, 1925). The thermomagnetic analysis of the Tawallah Valley ataxite (Fig. 4) is typical of most nickel-rich ataxites with curves (1) and (2) heating curves, while (3) and (4) are cooling curves. Curve (1) illustrates the behaviour of a previously unheated sample of the unaltered interior of the Tawallah Valley ataxite during thermomagnetic analysis from which the following phases may be identified.

(i) A discontinuity in the slope of the curve at 130 ± 20°C is identified as a γ-phase iron alloy containing 27 ± 3 per cent nickel. This is apparently the γ-phase alloy which surrounds the coarse α-bodies described previously.

(ii) A discontinuity at 320 ± 10°C which corresponds to the Curie point measured for a sample of schreibersite from the Mungindi fine octahedrite.

(iii) An unstable region X–Y in which the α_2-phase of the matrix decomposes.

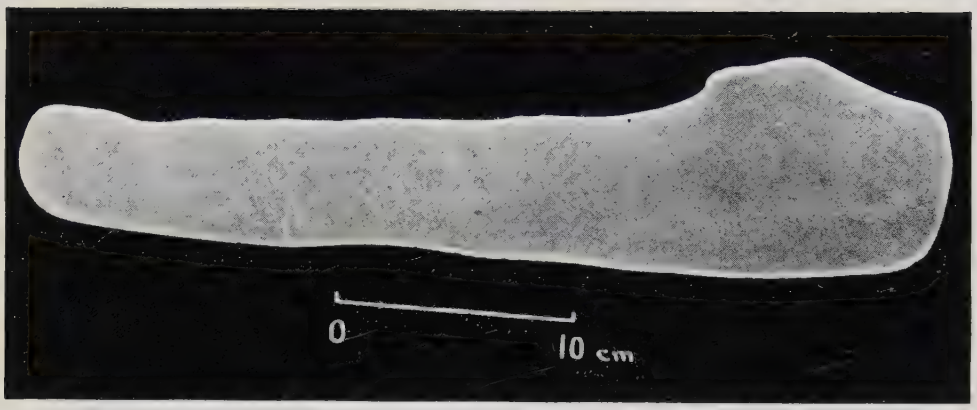

Fig. 1. Etched section of the Tawallah Valley nickel-rich ataxite showing thermal alteration rim.

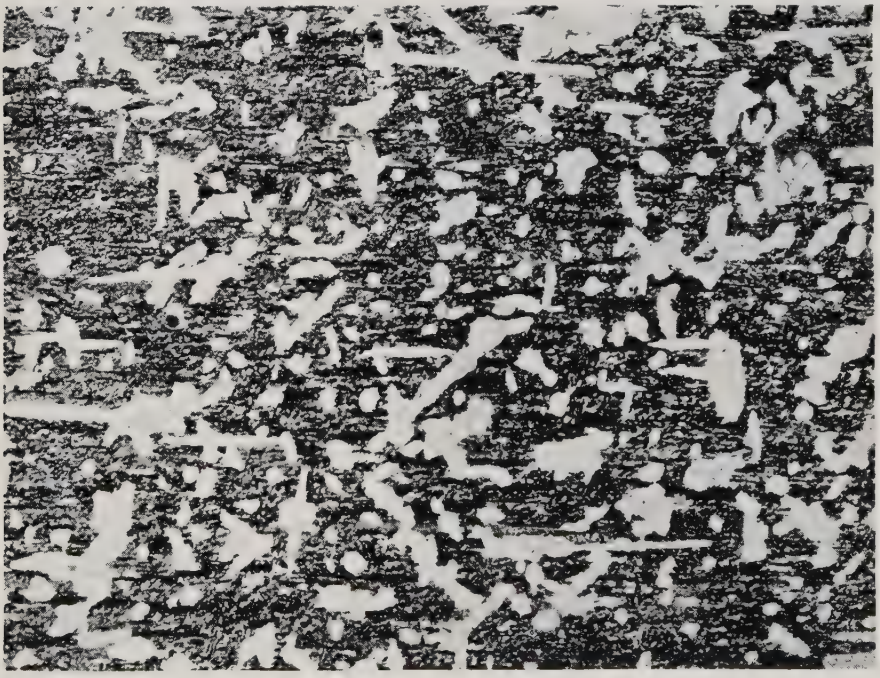

Fig. 2. Tawallah Valley—microstructure of unaltered interior. Etched. × 100.

Fig. 3. Tawallah Valley—microstructure of thermal alteration rim and fusion crust. Etched, ×100.

The shape of the curve in the region X–Y may be changed by varying the rate of heating. For example the dotted lines between curves (1) and (2) were obtained after the sample had been heated to 580°C for 30 min.

(iv) A discontinuity at 755 ± 5°C due to the transition of 7 ± 1 per cent nickel in iron α-phase alloy to γ-phase alloy. This phase is identified as the α-phase making up the coarse α-bodies described previously.

Curve (3) is the cooling curve following on the heating curve (1) and the changes

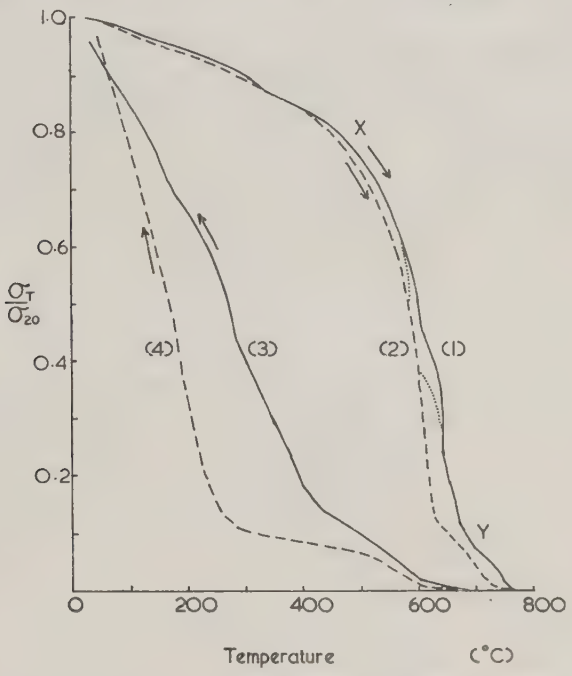

Fig. 4. Thermomagnetic analysis of the Tawallah Valley nickel-rich ataxite showing heating (1) and cooling (3) curves for previously unheated material and heating (2) and cooling (4) curves for material previously heated to 720°C for 60 min.

in slope are due to γ to α-phase transitions and which generally confirm the identifications above.

Curve (2) was obtained from a sample of the Tawallah Valley ataxite which had been heated at 720°C for 60 min. Thermomagnetic analysis indicates that this heat treatment, followed by slow cooling, has stabilized the α_2-phase by forming a normal α-phase containing 16 ± 2 per cent nickel. This α-phase is close to the overall nickel content of the Tawallah Valley ataxite reported by Lovering *et al.* (1957) as 18·2 per cent nickel. The heat treatment has also apparently caused a slight nickel enrichment in the low (i.e. 7 per cent) nickel α-phase alloy. Curve (4) is the cooling curve for this heat-treated sample. Table 1 is a summary of the magnetic phases present together with estimates of the relative amounts of each phase in the sample examined.

Thermomagnetic analysis of the Wedderburn ataxite gives results which are substantially similar to those obtained for the Tawallah Valley ataxite.

Thermal gradients in alteration rims

The thermomagnetic data can be used to estimate the lowest temperature at which the α_2-phase begins to decompose in the heated rims of both these nickel-rich ataxites. This temperature is taken to be operating at the inner boundary of the heated rims and melting temperatures (i.e. about 1480°C) are assumed at the outer boundary (i.e. the fused crust).

In the Tawallah Valley ataxite permanent compositional change is initiated *slowly* as soon as the temperature reaches 500°C, while at 680°C the relatively rapid

Table 1. Thermomagnetic analysis of the magnetic phases present in the Tawallah Valley nickel-rich ataxite

Characteristic Curie or transition temperature (°C)	Phase present (wt. % Ni)	Amount of phase present (wt. %)
130 ± 20	γ-phase nickel–iron alloy (27 ± 3% Ni)	4 ± 2
320 ± 10	Schreibersite $(Fe{\cdot}Ni)_3P$	trace
600 — 680	Decomposition of α_2-phase nickel–iron alloy	Major phase
755 ± 5	α-phase nickel–iron alloy (7 ± 1% Ni)	15 ± 5

transition of the α_2-phase to γ-phase is complete. Considering the short times involved in the formation of the heated rim during the flight of the meteorite through the atmosphere (probably less than 5 sec), the inner boundary of the heated rim represents a region in which rapid and substantial decomposition of the α_2-phase is taking place. The thermomagnetic data indicate that under these circumstances a temperature of about 680°C would be indicated for the inner boundary of the alteration zone.

The thermomagnetic data for the Wedderburn ataxite indicate that the α_2-phase has also undergone very substantial change at 650° and this is taken to be the lowest temperature at which substantial change in appearance of the structure of the meteorite can occur. This is in agreement with the thermal gradient estimated in the altered rim of the Tawallah Valley ataxite.

Theoretical Calculations of Rates of Ablation

The preceding discussion essentially establishes the temperatures at two depths in a nickel-rich ataxite at the end of its flight. Firstly, the surface temperature of the solid material during ablation in the atmosphere is the melting temperature, since the presence of a thin fused crust indicates that melting definitely took place, whatever the mechanism of removal of the melted material might be. Secondly,

it has now been established that the base of the thermal alteration rim indicates the depth to which a certain temperature (in the present case about 650°C) penetrated during flight. If it is assumed that ablation takes place at a constant rate during the portion of the flight through the atmosphere in which ablation takes place, the above information allows this rate to be estimated very simply for an iron meteorite of reasonably large size (say, with least diameter >1·5 cm). The method has the advantage of making no assumptions about the law of heat transfer to the meteorite.

For a reasonably large meteorite, and with the short times involved, curvature of the surface may be ignored and the meteorite treated as the semi-infinite solid $x > 0$ whose surface at which ablation takes place is the plane $x = 0$, so that this surface is maintained at the melting temperature v_0, and the solid is regarded as moving towards this surface with (unknown) speed U, which is assumed to be constant. The temperature v at depth x in the solid then satisfies the equation of conduction of heat in a moving medium [Carslaw and Jaeger, 1959, section 15·2(1)]

$$\frac{\partial^2 v}{\partial x^2} + \frac{U}{\kappa}\frac{\partial v}{\partial x} - \frac{1}{\kappa}\frac{\partial v}{\partial t} = 0 \qquad (1)$$

where $\kappa = K/\rho c$ is the thermal diffusivity of the solid, K being its thermal conductivity, ρ its density and c its specific heat. This equation has to be solved with $v = v_0$, when $x = 0$ and, for an initially cold body, $v = 0$°C when $t = 0$ and when $x \to \infty$. Actually the initial temperature of the meteorite will be determined by its heat balance with solar radiation and is probably about 4°C (Watson, 1956). When the ablation process has gone on for a sufficiently long time, steady conditions will be reached so that $\partial v/\partial t = 0$ in (1) and the temperature is given by

$$v = v_0 \exp(-Ux/\kappa) \qquad (2)$$

This is the result which will be used to estimate U; it will be shown later that it is adequate. The values $\rho = 8{\cdot}1$, $c = 0{\cdot}116$, $K = 0{\cdot}05$, $\kappa = 0{\cdot}0532$, $v_0 = 1480$°C for an 18 per cent nickel–iron alloy (Marsh, 1938) all units being c.g.s., calories and degrees Centigrade, will be used. For both the ataxites examined, the temperature at the base of the alteration zone seems to have been about 650°C and the average depth of the zone is 0·25 cm. Taking $v = 650$°C and $x = 0{\cdot}25$ in (2), together with the other values given, U is found to be 0·18 cm/sec.

The actual rate of ablation will vary both during the time of flight and over the surface of the meteorite, and (2) must be regarded simply as giving a rough average value. With regard to variation over the surface, it follows from (2) that, for given v, v_0 and κ, Ux is constant, so that the depth of alteration varies inversely as the rate of ablation and the thinnest alteration rims may be expected beneath the parts of the surface at which ablation is most rapid.

In this connexion it is of interest to consider the depth of the alteration rim which would form if the surface were maintained at the melting temperature but without ablation, as happens, for example, at sites at which a pool of molten metal collects. If the semi-infinite solid $x > 0$ is initially at zero temperature and its

surface $x = 0$ is maintained at temperature v_0 for a time t, the temperature v at depth x is given by Carslaw and Jaeger, 1959, section 2·4(10)

$$v = v_0 \operatorname{erfc} \frac{x}{2(\kappa t)^{1/2}} \tag{3}$$

where

$$\operatorname{erfc} x = \frac{2}{\pi^{1/2}} \int_x^\infty \exp(-y^2)\, dy, \quad \operatorname{ierfc} x = \int_x^\infty \operatorname{erfc} y\, dy \tag{4}$$

Taking $v_0 = 1480$°C (the melting temperature), $v = 650$°C (the temperature at the base of the alteration zone), $\kappa = 0{\cdot}053$ as before and $t = 4$ sec (a rather long time

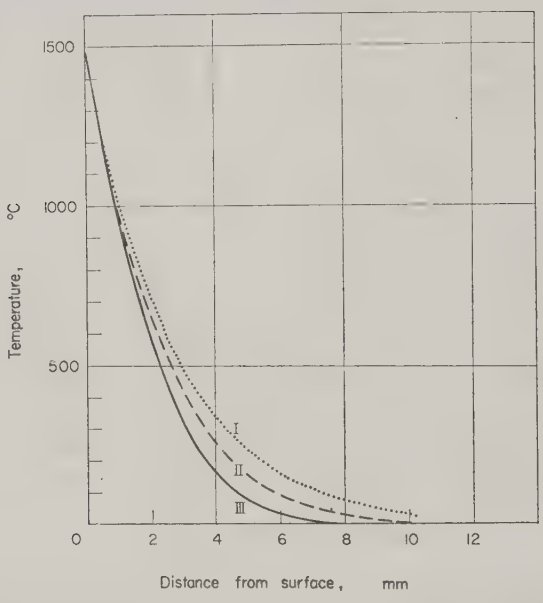

Fig. 5. Temperature distributions in outer regions of iron meteorites during ablation in the atmosphere. Curve I: the steady-state temperature distribution. Curve II: the unsteady state for zero initial temperature after 3 sec heating. Curve III: the temperature distribution after heating by constant flux for 1 sec.

of flight to allow for some pre-heating, see (iii) below), (3) gives $x = 0{\cdot}5$ cm, so that the depth of the alteration rim in a region in which no ablation is taking place, or beneath a pool of molten metal, is about twice the measured average value of 0·25 cm.

It is now necessary to consider the applicability of the simple steady-state result (2) to the more complicated situation which obtains in practice. Five points arise which will be considered in order: (i) the effect of the size of the meteorite; (ii) the question of whether the steady state has in fact been attained; (iii) the effect of heating in the atmosphere before the surface temperature reaches the melting point; (iv) the effect of penetration of heat from the rim into the interior after ablation has ceased; and (v) the effect of heating caused by impact with the earth's surface.

(i) *Size of the meteorite.* Curve I of Fig. 5 shows the variation of the steady-state temperature (2) with depth below the surface calculated for the numerical values

of U,κ and v_0 obtained above. It appears that the penetration of heat is negligible for depths greater than 1 cm so that the application of (2) to relatively large bodies is justified (it is, of course, completely inapplicable to bodies of millimetre dimensions).

(ii) *The unsteady state.* If the body is initially at 0°C and its surface is suddenly raised to temperature v_0 at time $t = 0$, the solution of (1) under these conditions is given by Carslaw and Jaeger, 1959, section 15·2(7)

$$v = \tfrac{1}{2}v_0\left[\operatorname{erfc}\frac{x+Ut}{2(\kappa t)^{1/2}} + \exp(-Ux/\kappa)\operatorname{erfc}\frac{x-Ut}{2(\kappa t)^{1/2}}\right], \tag{5}$$

where erfc x is defined in (4). Curve II of Fig. 5 shows the temperature distribution for the numerical values previously used, viz. $v_0 = 1480$, $U = 0{\cdot}18$, $\kappa = 0{\cdot}053$, and for $t = 3$ sec, that is, at the end of a rather short time of flight. It appears that in this rather extreme case the steady state has almost been attained.

(iii) *The effect of pre-heating.* Some heat will be conducted into the meteorite before it commences to melt at the surface. If it is assumed that heat is supplied to the surface at a constant rate during this early stage and that the surface reaches the melting temperature v_0 after time t_0, the temperature distribution at this time is given by Carslaw and Jaeger, 1959, section 2·9(6):

$$v = v_0\pi^{1/2}\operatorname{ierfc}\frac{x}{2(\kappa t_0)^{1/2}} \tag{6}$$

where ierfc x is defined in (4).

This temperature distribution for a time $t_0 = 1$ sec is shown in curve III of Fig. 5 and is seen to be very similar to the steady-state distribution, curve I. Thus pre-heating for a short time of 1 or 2 sec has the effect of establishing a temperature distribution very similar to that of the steady-state regime which may thus be regarded as being in operation during the whole of the observed time of flight.

(iv) *Penetration of heat after ablation ceases.* When the meteorite has fallen into the lower atmosphere it may be that the heat transfer to it from the air is insufficient to maintain the melting temperature at the surface and so ablation ceases. If the law of heat transfer to the surface during this part of the flight were known, temperatures in the meteorite could be calculated starting from the initial temperature distribution (2). In the absence of knowledge of this law, it is simplest to assume that there is no heat transfer to the meteorite during this part of the flight and to examine the consequences of this assumption. The temperature at any point and time may be calculated (Carslaw and Jaeger, 1959, Section 2·2(6)) and the surface temperature at time t_0 after ablation ceases is found to be

$$v_0\exp(U^2t_0/\kappa)\operatorname{erfc}U(t_0/\kappa)^{1/2} \tag{7}$$

With the previous values, namely $v_0 = 1480$, $\kappa = 0{\cdot}053$, $U = 0{\cdot}18$, this implies that the surface temperature will have fallen to 730°C after 1 sec and to 590°C after 2 sec. It can also be shown that the 650°C isothermal will move inwards from 2·5 mm to 2·9 mm, a change which is not important in view of the present uncertainties. If the heat transfer to the meteorite during this stage of flight is

such that (7) is an underestimate of the surface temperature, the penetration, of course, would be greater and the value of U obtained earlier would be an underestimate.*

(v) *The effect of heating during impact.* For a tabular body (such as the Tawallah Valley iron) of thickness D the kinetic energy at impact is $D\rho V^2/4J$ cal per unit surface area, where V is its velocity of impact and J is the mechanical equivalent of heat. If a fraction α of this energy is instantaneously converted to heat in the surface of the meteorite the temperature at depth x will rise by a maximum amount Δv given by

$$\Delta v = \frac{\alpha D V^2}{2Jcx(2\pi e)^{1/2}} \tag{8}$$

The velocities of impact of meteorites are very uncertain but observations by Hadding (1940) and calculations by Gustafson (1940) have both shown that the impact velocity of meteorites of average size is of the order of 10^4 cm/sec. Using this value for the Tawallah Valley meteorite with $D = 6$ cm and $\alpha = \frac{1}{2}$ it follows from (8) that the rise in temperature on impact at a depth of 2·5 mm is 30°C. It follows that heating on impact probably does not affect the position of the alteration rim.

Mass-Losses from Iron Meteorites during Ablation

It is difficult to estimate the period of time during which meteorites are ablated in the atmosphere. If it is assumed that the time during which meteorites are ablated is equivalent to their time of visual flight through the atmosphere, then ablation times are about 3·3 sec (La Paz, 1952). Given the rate of ablation U is 0·18 cm/sec, then an average depth of 0·6 cm has been removed from the surfaces of the Tawallah Valley and Wedderburn ataxites by ablation. From the present dimensions of the Wedderburn ataxite (Edwards, 1953), this amount of ablation corresponds to a mass-loss of about 60 per cent relative to the pre-atmosphere mass of the meteorite.

The mass-loss of the larger Tawallah Valley ataxite is more difficult to assess, mainly because its shape is rather irregular. According to Hodge-Smith and Edwards (1941), this slab-shaped meteorite was oriented in the atmosphere so that its longest dimension was parallel to the direction of flight. The section examined in the work (Fig. 1) was cut about half-way along the meteorite but parallel to the front surface and normal to the direction of flight. Consequently the ablation estimates given previously refer only to the ablation at the top, bottom and side surfaces about half-way along the length of the slab. Presumably

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* *Note added in proof*—We are indebted to Dr. J. R. Baxter of the Weapons Research Establishment, Salisbury, South Australia, for further discussion of this point. He estimates that after ablation ceases the surface temperature will fall from 1480°C to 600°C in about 2·5 sec. If this fall in temperature is assumed to be linear, calculations with the constants used previously show that the 650°C isothermal would move inwards from 2·5 mm to 3·5 mm: if this is the case then our estimate of the velocity of ablation would have to be increased by about 40 per cent. Dr. Baxter also points out that in meteorites with rippled surfaces the heat transfer rate, after ablation ceases, would be much lower in the depressions so that the above effect would be much less important at such places. On the other hand the depressions themselves have probably been formed by exceptionally rapid melting ablation so they might be expected to show relatively thin alteration rims.

considerably greater amounts of material were ablated from the surface closer to the head and less material was ablated from those surfaces closer to the rear. Under these circumstances it is probably not unreasonable to suggest that the figure calculated above for the amount of material removed during ablation approximates that of the average thickness lost from the surface of the slab. The dimensions of the Tawallah Valley ataxite have been reported by HODGE-SMITH and EDWARDS (1941), and from these data approximately 27 per cent of the pre-atmospheric mass of the Tawallah Valley ataxite has been lost by ablation.

Previous estimates of mass losses during ablation

C. A. BAUER (reported by THOMAS and WHIPPLE, 1951) examined the range of cosmic rays in iron meteorites together with the formation of helium-3 within those meteorites and estimated that the mass lost by iron meteorites during an atmospheric ablation was probably not greater than 90 per cent of their pre-atmospheric mass. MARTIN (1953), estimated mass-losses by ablation of spherical meteorites as a function of their terrestrial velocities using a formula derived by WHIPPLE and his collaborators and found that those with minimum terrestrial velocities (i.e. about 11 km/sec) should lose about 54 per cent of their pre-atmospheric mass by ablation while those with terrestrial velocities greater than about 30 km/sec should be virtually completely destroyed in the atmosphere. The mean terrestrial velocity of meteorites is probably about 24 km/sec corresponding to a mass-loss of about 96 per cent. MARTIN (1953) also reported that calculations by WEGENER of the terrestrial velocity of the Treysa medium octahedrite (19·8 km/sec) would indicate a mass-loss of about 90 per cent in the atmosphere. This was in good agreement with a 90 per cent mass-loss for this meteorite calculated on the basis of the central helium content of the meteorite also given by MARTIN (1953).

FIREMAN (1958b) determined the distribution of helium-3 in the Carbo octahedrite and concluded that 2 in. of metal must have covered the present surface where helium-3 values are highest and a much thicker layer where helium-3 is lower. A similar study on the Grant octahedrite (FIREMAN, 1959) indicated that about 45 per cent of the extra-terrestrial mass of the meteorite must have been removed to form the present shape of the meteorite. The mass-losses estimated for the Carbo and Grant octahedrites may not only be due to ablation in the atmosphere but may also include material removed by mechanical fracturing in the atmosphere. A more serious matter is the possibility of considerable terrestrial weathering of the surfaces of these meteorites since both are finds and may have been lying on the earth for many thousands of years. Indeed FIREMAN (1958a) measured the argon-39 content of the Carbo meteorite and concluded that this meteorite must have fallen more than 1500 years ago.

Calculations of the mass-losses of two nickel-rich ataxites based on their rate of ablation calculated from the thermal gradients in their alteration rims, accentuate the point that ablation of meteorites is a surface effect. This follows from the observation that a small meteorite (e.g. the Wedderburn ataxite) loses a greater proportion of its pre-atmospheric mass by ablation (i.e. about 60 per cent) than does a large meteorite (e.g. the Tawallah Valley ataxite with about 27 per cent mass-loss).

Summary

Many iron meteorites have narrow rims under their fused crusts in which their interior structures have been altered by heating during ablation in the earth's atmosphere. These thermal alteration rims are known to occur in all major structure classes of iron meteorites (e.g. hexahedrites, octahedrites and ataxites) but for most it is difficult to make a quantitative estimate of the thermal gradients existing in these alteration rims.

Thermal alteration rims occurring on the Tawallah Valley and Wedderburn nickel-rich ataxites are shown to be formed by the decomposition of metastable α_2-phase alloy during heating in the atmosphere. The depths of the rims range from about 1 mm to 4 mm and average 2·5 mm. Calculations indicate that if the shape of a meteorite is such that molten pools of ablated crustal material can collect on the rear surfaces, then alteration rims under these surfaces may be twice as deep as the average depth under front surfaces where ablation is taking place. Thermomagnetic analysis of the Tawallah Valley and Wedderburn ataxites has shown the manner in which the α_2-phase decomposes during heating and the temperature existing at the inner boundary of the alteration zone during flight in the atmosphere (i.e. about 650°C). Given that the surface temperature is the melting temperature for the meteorites (i.e. about 1480°C), and assuming steady-state conditions for the ablation of the meteorites, then the rate of ablation of the outer surface of the iron meteorites has been calculated as about 0·18 cm/sec. If the average time during which meteorites are ablated in the earth's atmosphere is about 3·3 sec, then an average depth of 0·6 cm has been removed from each meteorite. These data indicate that the Tawallah Valley ataxite has lost about 27 per cent of its pre-atmospheric mass and the Wedderburn about 60 per cent.

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The estimation of the oxidation state of pitchblende in ores

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Abstract—The uranyl fluoride content of fully hydrofluorinated uranium oxides, whether pure or mixed with the oxides of a number of other metals, is a practical measure of the original U^{VI} content. This observation forms the basis for determining the oxidation state of pitchblende when more precise methods are inapplicable. Metallic and carbonaceous contamination must be absent, and the sulphide content of the ore must be reduced to the level of a few per cent relative to the uranium content, by means of ore-dressing techniques. The method involves reacting the finely ground concentrate to constant weight with anhydrous hydrogen fluoride gas at a maximum temperature of 350°C in a thermobalance modified for work with corrosive gases. Uranyl fluoride is leached from the product with cold saturated aqueous sodium fluoride, and uranium tetrafluoride is dissolved from the residue with hot ammonium oxalate solution. In each case, the extracted uranium is determined either spectrophotometrically or fluorimetrically. Application to problematical ores other than pitchblende, such as davidite, is envisaged.

1. Introduction

Earlier reports from this laboratory (Stonhill, 1958, 1959a, b) have described methods for the determination of the oxidation state of uranium in its commercially or experimentally produced oxides. These methods depend either on the dissolution of the material in 50% phosphoric acid followed by titration of hexavalent uranium with titanous sulphate, or on successive thermogravimetric oxidation and reduction whence the molecular formula (i.e. oxygen–uranium atomic ratio) is derived. These methods are subject to interference arising from the presence of elements which, on dissolution, react with the uranium to change its valency state, or are themselves titrable, or are capable of reacting with oxidizing or reducing atmospheres. Pitchblende ore from the Beaverlodge, Saskatchewan, area, the subject of the present investigation, presents special analytical problems of these types because of its intimate association with a wide variety of minerals, quantitatively minor uranium content (of the order of 0·2 per cent calculated as U_3O_8), and difficult solubility. The order of abundance of the most important constituents are, according to Robinson (1955):

haematite	Fe_2O_3	clausthalite	PbSe
pyrite	FeS_2	bornite	Cu_5FeS_4
pitchblende	UO_X	nolanite	$Fe_3V_8O_{20}$
chalcopyrite	$CuFeS_2$	ilmenite	$FeTiO_3$
galena	PbS	marcasite	FeS_2
		sphalerite	ZnS

The possible complexity of pitchblende is evident from the study of Kidd and Haycock (1935), who detected forty metallic minerals in Port Radium (North West Territories) ore.

In the course of X-ray diffraction studies a change of pattern with increasing

oxidation has been noted (Brooker and Nuffield, 1952: Berman, 1957: Sidorenko, 1958) but no determinative method has been described. In much early work UO_2/UO_3 ratios are stated without any indication of the method used to determine them, but it may be presumed that the investigators dissolved their pitchblende in acid solution and titrated tetravalent uranium with potassium permanganate, as did Gledisch and Bakken (1937) in their work with a single crystal of uranium oxide. A number of similar chemical procedures are standard (Rodden, 1950) intended mainly for simple materials. Brooker and Nuffield (1952) rejected this volumetric method for samples containing iron and instead, proposed dissolution of the ore in hydrofluoric acid at 50–60°C in a stream of nitrogen over a period of 4 days with subsequent separation of soluble uranyl fluoride from insoluble uranium tetrafluoride. Apart from the length of time needed, application of this method to the problem in hand would be of little use because interactions can still occur in solution. For example, in presence of fluoride ion, Fe^{II} will reduce hexavalent uranium. Further objection may be raised on the ground that formation of an initial deposit of insoluble UF_4 on unreacted pitchblende makes complete reaction uncertain. The only rigorous analytical investigation into the effect of reactive concomitants on the determined oxidation state of uranium in natural materials appears to be that of Clarke and Altschuler (1958) relating to apatite and phosphorite. Their method, based on dissolution of the minerals in dilute phosphoric acid at 5°C, is inapplicable to Beaverlodge pitchblende ore (and probably most, if not all, others) which requires treatment with hot nitric, sulphuric and hydrofluoric acids to obtain an analytical solution. Under such conditions, the number of possible interactions involving iron, vanadium, sulphides etc., precludes any direct dissolution method, and a less direct approach is necessary at some expense in precision. Information so obtained has a bearing on the efficiency of the alkaline leaching process of uranium recovery (Forward and Halpern, 1954). The method recommended here avoids valency changes by controlled conversion of the uranium oxides in the pitchblende to their fluorides under anhydrous conditions. These fluorides can easily be leached from accompanying impurities.

In the following discussion, pitchblende will be considered to be a mixture of the oxides of tetravalent and hexavalent uranium in varying proportions within the limits UO_2 and U_3O_8. The assumption is made that conclusions drawn using synthetic oxides are applicable to oxides of natural occurrence.

2. Apparatus

Use was made of a thermobalance modified for use with hazardous atmospheres (Stonhill, 1959a,b).

3. Experimental

Pure uranous and uranic oxides react stoichiometrically with gaseous hydrogen fluoride to form uranium tetrafluoride and uranyl fluoride respectively:

$$UO_2 + 4HF = UF_4 + 2H_2O$$

$$UO_3 + 2HF = UO_2F_2 + H_2O$$

Kuhlman (1949) observed that uranous-uranic oxide reacts with hydrogen fluoride gas as if it were a mixture in the proportion one molecule of uranous oxide to two molecules of uranic oxide:

$$U_3O_8 + 8HF = UF_4 + 2UO_2F_2 + 4H_2O$$

and the work of Susic (1953) with aqueous hydrofluoric acid and pure uranium oxides of various oxygen–uranium ratios indicates that valency ratios are essentially unaltered by conversion to fluorides. In our own work, it was necessary to establish the same principle as applied to gaseous hydrogen fluoride, not only with pure oxides but also with mixed uranium and other metal oxides, and sulphides, to simulate the essential chemical nature of pitchblende ore.

Table 1. Recovery of hexavalent uranium as uranyl fluoride after hydrofluorination of pure uranium oxides

Sample type	U^{VI} content of sample as detd. by titration (Wt. %)	Hexavalent U recovered expressed as U^{VI}	
		As % of original sample weight	As % of U^{VI} content of original sample
Partly reduced UO_3	11·6	9·44	81·3
Partly reduced UO_3	21·7	23·4	108
Partly reduced UO_3	31·7	27·2	85·8
U_3O_8 (99·9%)	56·6	48·3	85·4
Partly oxidized UO_2	7·73	8·58	111
Partly oxidized UO_2	14·3	14·1	98·3
Partly oxidized UO_2	17·4	14·6	84·0
Partly oxidized UO_2	24·8	26·8	108
Partly oxidized UO_2	28·9	33·8	117
		Standard deviation	13·8

The data in Table 1 show that the original oxidation state can be reasonably estimated from the uranyl fluoride content of the fully reacted product, bearing in mind the purpose of the investigation.

3.1. *Hydrofluorination of pure uranium oxides*

A number of partly reduced orange oxide powders and somewhat oxidized brown oxide samples were hydrofluorinated, and the products analysed for uranyl fluoride content, according to the procedures described in a later section.

The uranyl fluoride values so obtained were compared with the values expected from the oxidation state of the starting materials as determined via their molecular formulae. The comparisons are given in Table 1.

3.2. *Hydrofluorination of impure uranium oxides*

3.2.1. *Hydrofluorination after addition of other metal oxides.* Haematite, Fe_2O_3, preponderates over pitchblende in the ore under consideration, and an investigation into the effect of this oxide, together with other oxides whose presence would invalidate alternative oxidation-state methods, was made. The

choice of a number of the oxides added was suggested by the problems associated with them rather than their known occurrence in ore.

Two oxides, $UO_{2\cdot66}$ and $UO_{2\cdot41}$, were used as carriers in these experiments. Mixtures were prepared of equal parts by weight of the carrier and the oxide under test, the constituents being pulverised separately to pass a fine screen (300-mesh was usually employed), then mixed together in a rotary blender with addition of an equal weight of magnesium fluoride powder to counteract any tendency to sinter during hydrofluorination. As before, the hydrofluorination and analysis for uranyl fluoride was carried out as set forth under the analytical methods heading, and for the purpose of calculating the expected uranyl fluoride contents of the products, the weight change attending hydrofluorination was taken from the thermogravimetric record. Incidental information was obtained regarding the behaviour of the added oxides, and this is recorded, together with the effect of each oxide on uranyl fluoride recoveries, in Table 2.

Table 2. Recovery of uranyl fluoride from mixtures of uranium oxides and other metallic oxides

Oxide added	UO_2F_2 recovered (%)		Reaction of added oxide during hydrofluorination
	From $UO_{2\cdot67}$	From $UO_{2\cdot41}$	
Sb_2O_3	101·5	90·0	slow
Sb_2O_5	91·0	94·5	rapid loss at 200°C
As_2O_3	88·5	95·5	rapid loss at 100°C
As_2O_5	181·0	242·0	continuous loss
Bi_2O_3	90·5	91·0	none
CeO_2	104·0	129·0	slow
Cr_2O_3	88·2	98·2	none
CuO	53·0	50·0	none
FeO	4·0	1·7	slow
Fe_2O_3	84·0	97·3	none
$FeTiO_3$	100·4	80·0	none
PbO_2	88·0	93·5	none
Pb_3O_4	77·3	89·5	slow
MnO_2	101·0	120·0	none
NiO	86·6	97·7	slow
SeO_2	95·7	100·0	all lost at 200°C
SnO	0·3	1·7	slow
WO_3	85·5	98·0	slow loss above 300°C
V_2O_5	89·3	95·5	all lost at 100 to 150°C
ZrO_2	76·0	81·1	fast reaction above 250°C
Standard deviation (disregarding results with As_2O_5, FeO, CuO, and SnO	8·3	13·8	
	Standard deviation from both sets of results: 11·3%		

From the data in Table 2, a high concentration of quite a number of oxides has little effect on the conversion of hexavalent uranium to uranyl fluoride. Manganese and lead dioxides, and arsenic pentoxide, which tend to liberate oxygen in presence of hydrogen fluoride cause an increase in the uranyl fluoride value while strong reductants such as ferrous and stannous oxides have the opposite effect. It is noteworthy that ilmenite, $FeO.TiO_2$, does not have this reducing action, and that the volatility of the fluoride reaction products of selenium, arsenous and vanadic oxides conveniently removes some otherwise troublesome compounds at quite low temperatures. It is concluded, then, that at concentrations up to 50 per cent, oxides, other than those of a particularly reactive character which are involatile in hydrogen fluoride, will not interfere in the method, since the overall standard deviations in Tables 1 and 2 are similar.

3.2.2. *Hydrofluorination with sulphide additions.* Pitchblende deposits are invariably associated with sulphides, predominantly pyrite. Typically, Beaverlodge

Table 3. Influence of temperature on recovery of hexavalent uranium as uranyl fluoride from 50–50 mixtures of U_3O_8 and pyrite

Temperature maximum (°C)	Hexavalent uranium recovered as % of U^{VI} content of original mixture
400	1·8
350	6·8
300	10·1
250	29·7

ore contains about four times more total sulphide (expressed as sulphur) than uranium, and experiments in which uranium oxides were hydrofluorinated in admixture with 50% pyrite showed, by the resultant very poor uranyl fluoride recoveries, that the main limitation of the method would be encountered at this stage. Even when the maximum temperature was decreased to 250°C, the lowest at which a reasonable reaction rate was attained, recoveries were still unsatisfactory as Table 3 shows.

As an alternative, the maximum tolerable pyrite concentration for acceptable uranyl fluoride recovery at a reaction temperature not exceeding 350°C was determined. Table 4 shows that pyrite should not be present in a binary mixture much in excess of 2 per cent by weight. It will be shown below that in a multicomponent mixture the tolerance to pyrite is greater.

It is concluded from this section of the investigation that pitchblende ore must be beneficiated in uranium at the expense of sulphides if a successful oxidation-state analysis is to be possible.

3.2.3. *Hydrofluorination of pyrite–metal oxide–uranium oxide mixtures.* To extend data from the preceding sections beyond two-component mixtures, to simulate in a general way the kind of mixtures which might be encountered with an actual ore concentrate, and to ascertain that the consequent dilution of the pyrite and uranium constituents gives greater tolerance of pyrite, a mixture of

equal weights of haematite, dolomite, vanadium pentoxide, bismuth trioxide arsenic oxide and ilmenite was prepared. Using this matrix, two experimental mixtures were made, one containing 10% $UO_{2\cdot41}$ and 3% pyrite, the other 10% $UO_{2\cdot41}$ and 6% pyrite. The usual procedures led to a U^{VI} recovery of 118 per cent of the expected value in the case of the former, and 82·2 per cent in the latter case. Taking account of the circumstances, these recoveries are satisfactory and provide additional evidence for the validity of the general method.

Table 4. Influence of pyrite content on recovery of uranyl fluoride from mixtures of U_3O_8 and pyrite at 350° C

U_3O_8: pyrite ratio	U^{VI} recovery, % of original U^{VI}
1 : 1	6·8
9 : 1	22·1
19 : 1	69·2
49 : 1	90·5

4. Preparation and Hydrofluorination of Pitchblende Concentrates

4.1. *Beneficiation to remove sulphides*

The most efficient technique for removing sulphides is to start with massive or and first remove obviously pyritic regions by drilling. Crushing and wet ball-milling with steel balls, followed by final up-grading on a Haultain super-panner, recovered roughly 50 per cent of the original uranium values from Ace and Verna Mine samples assaying some 0·2 per cent U_3O_8. No detailed investigation of the

Table 5. Analysis of pitchblende concentrates

Origin of ore	Pitchblende concentrate			
	U_3O_8 (%)	S (%)	S to U_3O_8 ratio	Oxidation state U^{IV} to U^{VI} ratio
Ace Mine, level 2 stope No. 301	52·2	0·24	0·005	3 : 1
Verna Mine, level 4 4B2, No. 7 stope	21·5	0·66	0·031	17 : 1

ore-dressing stage was made; the method of *U.S. Pat.* 2570120 could probably be used in this connexion.

Analysis of the uraniferous concentrates obtained (Table 5) shows that the total sulphur content can be reduced from approximately 400 per cent of the uranium content to levels acceptable for the hydrofluorination procedure.

There was no evidence of alteration of the pitchblende and therefore little danger that the 50 per cent recovery of uranium resulted in an unrepresentative sample.

4.2. *Concomitants of uranium in pitchblende concentrates*

After beneficiation of the ore as described above, microscopic examination revealed that the major constituents other than pitchblende itself were haematite, in the form of extremely fine veins, and gangue minerals identified as quartz and calcite. Important constituents found spectrographically were titanium and vanadium, probably representing ilmenite and nolanite, respectively.

On the evidence of the development work carried out, oxidation ratio findings will be unaffected by these materials. The Verna concentrate, as recorded in Table 5, contained nearly 6 per cent total sulphur calculated as pyrite, but the satisfactory processing of the synthetic mixture described in Section 3.2.3 as bearing 6 per cent pyrite indicates that the oxidation ratio reported for this ore is reliable.

4.3. *Effect of free metals and carbonaceous matter*

The presence of metallic iron was found experimentally to invalidate the method because of its reducing action. It is, however, unlikely that free metals would be encountered in ore, except by introduction in the ball-milling stage. Magnetic separation or dilute acid leaching would overcome this difficulty, and qualitative tests for such contamination are well-known.

Some minerals, notably thucholite, contain a large proportion of hydrocarbon, and the reducing action of these materials would interfere in the method. Such interference is not expected in the case of pitchblende, at least after beneficiation. The concentrates obtained in the present work contained less than 0·08 per cent carbon.

5. Analytical Methods

5.1. *Hydrofluorination procedure*

The object of the procedure to be described is fully to convert the uranium oxides in the ore to their fluorides at as low a temperature as possible. Complete conversion is critical since UO_3 reacts faster than U_3O_8 or UO_2, and moderation in the heat applied to the material is desirable in order to minimize solid-state reactions. A knowledge of the non-uranium constituents and their thermogravimetric behaviour, and a trial hydrofluorination up to a temperature of about 600°C, enable close control of the reaction to be exercised.

Pulverize sufficient of the sample to contain about 0·5 g uranium oxides so that the whole passes a 300-mesh sieve. Add an equal weight of magnesium fluoride and mix. Place the powder, contained in a platinum crucible, in the cold reaction tube of the thermobalance and purge with nitrogen or argon. Heat to 100°C.

Admit hydrogen fluoride gas, pure or diluted with an inert gas. Raise the temperature gradually to a maximum of 350°C, holding steady at any stage where the reaction is rapid before applying more heat. Keep the temperature at 350°C until the sample attains constant weight. (The procedure should be modified as necessary in the light of the principles stated above). Displace residual hydrogen fluoride with inert gas after completion of the reaction stage and cool the apparatus to 100°C by blowing air around the reaction tube. Remove the sample; pulverize in an agate mortar, and analyse as described below.

5.2. *The determination of* UO_2F_2 *and* UF_4 *in hydrofluorinated uranium oxides*

The principle of this assay has been stated in the earlier part of this report. Saturated sodium fluoride solution is used as the extractant for UO_2F_2, although it has been found that ethanol containing about 10 per cent water is equally useful. The dissolved uranium may often be determined directly in this solution, but, depending on the accompanying impurities, an ethyl acetate extraction is sometimes necessary. This extraction proceeds as below.

Reagents. Sodium fluoride, saturated aqueous solution; sodium hydroxide, 20 per cent w/v and 40 per cent w/v; hydrogen peroxide, 30 per cent w/v; aluminium nitrate, aqueous solution saturated at 130°C; ethyl acetate; ammonium oxalate, 5 per cent solution w/v.

Procedure. Transfer the whole of the hydrofluorinated sample (or a weighed part of this, if a particularly high uranyl fluoride value is expected) into a beaker and add 50 ml sodium fluoride solution.

Stir 15 min then filter and wash the residue with sodium fluoride solution. Make up to 250 ml. Take 25 ml of this solution, add 2·25 ml concentrated nitric acid, 35 ml aluminium nitrate solution at 130°C, and 20 ml ethyl acetate. Shake and discard the lower layer. Re-extract the uranium from the organic layer into two 15 ml volumes of water, and neutralize this extract with a 40% sodium hydroxide solution. Add 25 ml of a 20% sodium hydroxide solution and 2·5 ml. hydrogen peroxide, dilute to 250 ml and measure the optical density of the solution at 400 mμ on a spectrophotometer. Apply the calibration factor and calculate the amount of hexavalent uranium extracted as UO_2F_2 from the original sample.

To determine UF_4, reflux the residue from the sodium fluoride extraction with 50 ml ammonium oxalate solution. Filter, and make up the filtrate to 250 ml, then proceed as above. Alternatively the total uranium content of the original sample may be determined by any of the well-known methods, and tetravalent uranium calculated by difference using the hexavalent uranium result.

The oxidation state of the uranium in the ore may then be expressed either as the ratio $U^{IV} : U^{VI}$ or $UO_3 : UO_2$ as preferred. If the uranium content of the original sample is very low, a fluorimetric procedure can replace the spectrophotometric.

6. Scope and Applications of the Method

The value of the technique described lies in its applicability to cases where precise chemical methods fail, and it is in this respect supplementary to those methods. The investigation has demonstrated that the hexavalent uranium in complex oxide mixtures can be recovered as uranyl fluoride with an accuracy, at the 95 per cent confidence level, of ± 23 per cent.

This is comparable to the accuracy which under favourable circumstances might be achieved with the X-ray diffraction method applied to pitchblende. The foregoing method has the advantage of operating with a much larger amount of material, with a greatly decreased error of sampling. Also, being chemical in nature, the complications of the metamict state do not arise. Both methods require similar preparation, such as crushing and concentration.

The investigation was carried sufficiently far to show that the recommended method should be applicable to other uranium minerals, besides pitchblende, such as carnotite, uraninite, davidite, etc.

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The record in the meteorites—I

The former environment of stone meteorites as deduced from K^{40}–Ar^{40} ages†‡

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Abstract—The K–Ar ages of meteorites are systematically lower than the Rb–Sr and Pb–Pb ages, owing to diffusion losses of argon. An equation is derived that gives the apparent K–Ar age as a function of the "true" age and the parameter D/a^2, the diffusion constant of Ar^{40} divided by the square of the radius of the potassium-bearing grains. The dependence of D/a^2 in stone meteorites on temperature may be obtained from the work of Geiss and Hess, so that given a "true" and an apparent age, it is possible to deduce an upper limit to the mean temperature at which a meteorite was held since the cessation of strong heating in its parent body. The activation energy for the diffusion of radiogenic Ar^{40} from meteorites is unexpectedly small (14 kcal/mole), so that for a group of eight dated chondrites, the upper limit to the mean environmental temperature is found to be $\leqslant 196°K$. This low value implies that the parent body of the chondrites was no closer to the sun than 1·44 astronomical units (a.u.), and no larger than 250 km in radius, for radiation temperatures are higher near the sun, and long-lived radioactivities produce higher temperatures in bodies as large as 300 km in radius. The compatibility of these limits with current theories on the origin of meteorites is examined, and some crucial experiments are proposed.

Further diffusion losses will occur after the release of the meteorites from their parent bodies. Consideration of the radiation temperature of a meteorite in space shows that even for perihelia barely within the earth's orbit, some 10-20 per cent of the radiogenic and cosmic-ray induced argon will be lost in times the order of typical exposure ages of chondrites.

I. Introduction

Some of the most important dating techniques which have been applied to meteorites depend upon the noble-gas content of the specimen, notably the determinations of the K–Ar and U–He ages, the I^{129}–Xe^{129} age, and the cosmic ray exposure ages based on He^3, Ne^{21} and Ar^{38}. The ages thus obtained are reliable only if the meteorites have quantitively retained their noble gases. Systematic errors in these ages due to losses of noble gases, however, may of themselves provide additional information on the history of the meteorites. We shall demonstrate that a detailed consideration of argon diffusion losses gives such information on the past history and environment of the stone meteorites, and enables us to place highly restrictive limits on the size and former location of their parent bodies. In addition, we shall show that further diffusion losses of noble gases probably occurred after the break-up of these parent bodies, causing serious negative errors in the reported cosmic-ray ages.

II. The Effect of Diffusion Losses on K–Ar Ages

In contrast to the Pb–Pb and Rb–Sr ages which give the time of the last solidification of meteoritic phases, the K^{40}–Ar^{40} age determinations for meteorites seek the date of the most recent heating event intense enough to expel the entire content of argon. A number of meteoritic K–Ar ages have become available in the

† This work was supported in part by the U.S. Atomic Energy Commission.
‡ From heating experiments by Geiss and Hess (1958).

last few years through the exacting work of Gerling and co-workers (1951, 1955), Wasserburg and Hayden (1955a) and Geiss and Hess (1958). The dates of most chondrites lie in the range 4·0–4·4 aeons*, while those of achondrites extend from 4·4 down to 0·5 aeons (Table I). These may be compared with Pb–Pb and Rb–Sr ages which lie in the range 4·5–4·6 aeons (Patterson, 1956; Schumacher, 1956; Gast, 1959). Stoenner and Zähringer (1958) have suggested that the K–Ar ages may be systematically low due to continuous argon losses by diffusion during geologic time, as has been observed in the case of terrestrial feldspars (Wasserburg, 1954; Reynolds, 1957; Gentner and Kley, 1957). In order to explore this possibility, we must set forth a relationship between the true and the apparent K–Ar ages. This relationship depends only on a single diffusion parameter, which is a function of the temperature at which the meteorite has been held since the last total expulsion of its argon.

A. *The mathematical model for continuous diffusion losses*

We wish to derive an equation relating the apparent K–Ar ages to the rates of diffusion of argon in meteorites. It may be assumed that the rate-controlling step in the loss of argon is volume diffusion within crystal grains, rather than diffusion along grain boundaries. The magnitude of the losses depends on D, the diffusion coefficient of the K–bearing grains, and a, the radius of the grains, which we approximate as spherical.

The differential equation which determines the Ar^{40} concentration as a function of time is

$$\frac{\partial \mathbf{A}}{\partial t} = D\nabla^2\mathbf{A} + \varepsilon\lambda\mathbf{K}_0 \exp(-\lambda t) \tag{1}$$

in which $\mathbf{A}$ is the Ar^{40} concentration at any time, $\mathbf{K}_0$ is the initial K^{40} concentration, λ is the decay constant of K^{40}, and ε is the fraction of electron capture events, $K^{40} \xrightarrow{\text{e.c.}} Ar^{40}$, in the total number of decays. The competing decay mode, $K^{40} \xrightarrow{\beta^-} Ca^{40}$, destroys K^{40} but does not produce Ar^{40}. In spherical polar coordinates the diffusion equation is

$$\frac{\partial \mathbf{A}}{\partial t} = \frac{D}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial \mathbf{A}}{\partial r}\right) + \varepsilon\lambda\mathbf{K}_0 \exp(-\lambda t) \tag{2}$$

and the boundary conditions to be imposed on $\mathbf{A}(r,t)$ are the initial absence of argon, $\mathbf{A}(r,0) = 0$, and the rapid removal of argon from the surface of the grains (diffusion along grain boundaries), $\mathbf{A}(a,t) = 0$. This differential equation is obviously analogous to the equation governing temperature in a uniform, radioactively-heated sphere, with zero temperature initially and zero temperature at the boundary. The solution to the thermal problem is given by Urey (1952) and the solution to equation (2) is found by simple transformations of Urey's result. Thus:

$$\mathbf{A}(r,t) = \sum_{n=1}^{\infty} \frac{\varepsilon\lambda K_0}{\lambda - Dn^2\pi^2/a^2} \cdot \frac{2(-1)^n}{n\pi} \cdot \frac{a}{r} \sin\frac{n\pi r}{a} \left[\exp(-\lambda t) - \exp(-Dn^2\pi^2 t/a^2)\right] \tag{3}$$

* An aeon is defined as 10^9 years, following the suggestion by Urey (1957).

Table 1. Selected age determinations for stone meteorites

(A). Potassium-argon ages

Meteorite	Age* (aeons)	Cosmic-Ray age (millions of years)	References
Chondrites:			
Holbrook	4·40	27	1, 2
Bjurböle	4·32	17	1, 2
Beardsley	4·30	9	1, 2
Mocs	4·30		1
Richardton	4·15	33	1, 2
Marion	4·08		1
St. Michel	4·00	32	1, 2
Forest City	4·15		3
Crystalline Chondrites:			
Kunashak	0·7	4	4
Pyervomaiskii			
(black)	1·8		4
(grey)	0·65	6	4
Achondrites:			
Norton County	4·40		1
Pasamonte	3·80	9	1, 2
Frankfort	3·34		1
Moore County	3·23		1
Nuevo Laredo	3·1–3·6	5	5
Shergotty	0·56	5 (He^3); 11 (Ar^{38})	1, 2
Padvarninkai	1·0	20	4

* The reported errors in the K–Ar ages range from ~0·1 aeon to ~0·7 aeon.

(B) Phase separation ages*

Meteorite	Age (aeons)	Method	References
Nuevo Laredo	4·55 ± 0·17	Pb–Pb	6
Nuevo Laredo	4·4–4·6	Rb–Sr	8
Pasamonte	4·54 ± 0·21	Rb–Sr	7
Pasamonte	4·4–4·6	Rb–Sr	8
Sioux County	4·4–4·6	Rb–Sr	8

Key to References for Table 1

1. Geiss and Hess (1958).
2. Eberhardt and Hess (1959).
3. Wasserburg and Hayden (1955), recalculated by Geiss and Hess (1958).
4. Gerling and Levskii (1956).
5. Reynolds and Lipson (1957).
6. Patterson (1956).
7. Schumacher (1956), recalculated using the Rb^{87} half-life of Flynn and Glendenin (1959).
8. Gast (1959).

* The Rb–Sr ages denote the time when the Sr of the chondrites and of the achondrites had the same isotopic composition. If, as is commonly assumed, these two classes of meteorites are genetically related, this date is that of the differentiation of achondrites from chondritic-like material. The reference chondrites are Forest City and Richardton.

The total argon content A of a grain of radius a at any time t is

$$A = 4\pi \int_0^a r^2 \mathbf{A}(r,t)\, dr = \sum_{n=1}^{\infty} \frac{\varepsilon\lambda \mathbf{K}_0}{\lambda - Dn^2\pi^2/a^2} \cdot \frac{8\pi a^3}{n^2\pi^2} [\exp(-Dn^2\pi^2 t/a^2) - \exp(-\lambda t)] \tag{4}$$

The total K^{40} in a grain, K, is just

$$K = \frac{4}{3}\pi a^3 \mathbf{K} \tag{5}$$

and the change in the total quantity of K^{40} in each grain is governed by the simple radioactive decay law

$$\frac{dK}{dt} = -\lambda K \tag{6}$$

since there is no diffusive loss of potassium. We may integrate equation (6), using the symbol K_0 to denote the total abundance of K^{40} in a grain at the time when argon was completely driven off for the last time

$$t = \frac{1}{\lambda} \ln \frac{K_0}{K} \tag{7}$$

Under the assumption that there is *no* diffusive loss of argon, the "apparent age" of the meteorite t^* is found by replacing K_0 with $(K + (1/\varepsilon)A)$, since both K and A can be directly determined:

$$t^* = \frac{1}{\lambda} \ln \frac{K + (1/\varepsilon, A)}{K} \tag{8}$$

We now replace A in expression (8) with the quantity in expression (4) which was found by making allowance for diffusive losses. An equation relating t^*, the apparent age, to t, the true age, is the result:

$$t^* = \frac{1}{\lambda} \ln \left[1 + \sum_{n=1}^{\infty} \frac{\lambda}{\lambda - Dn^2\pi^2/a^2} \cdot \frac{6}{n^2\pi^2} \left\{ \exp\left(\lambda t - \frac{Dn^2\pi^2 t}{a^2}\right) - 1 \right\} \right]^{\dagger} \tag{9}$$

Equation (9) depends on D and a only in the combination D/a^2. It provides a means of correcting measured K–Ar ages for diffusion losses, provided an average value of the ratio D/a^2 is known for the meteorite. Fig. 1 compares the measured with the true ages of stone meteorites for several values of the parameter D/a^2. We shall next consider the highest values of D/a^2 which are consistent with other knowledge that has been obtained from meteorites, and will then discuss the temperature dependence of the parameter D/a^2 in meteorites.

B. *The "true age" of chondrites*

It is possible to set an upper limit on the true date of argon expulsion in stone meteorites by means of dates from the Pb^{206}–Pb^{207} or the Rb^{87}–Sr^{87} methods. The date obtained by the Pb–Pb method refers to the fractionation of lead from

† A solution of the diffusion equation in terms of the Ar^{40}/K^{40} ratio has already been published by Wasserburg (1954). An expression more closely related to our equation (9), in terms of t and t^*, was later derived by Nicolaysen (1957), but the present derivation is considerably simpler.

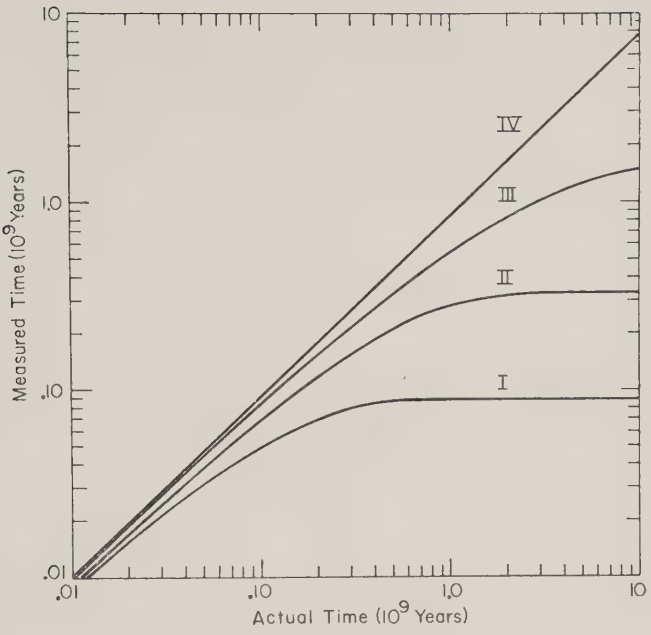

Fig. 1(*a*).

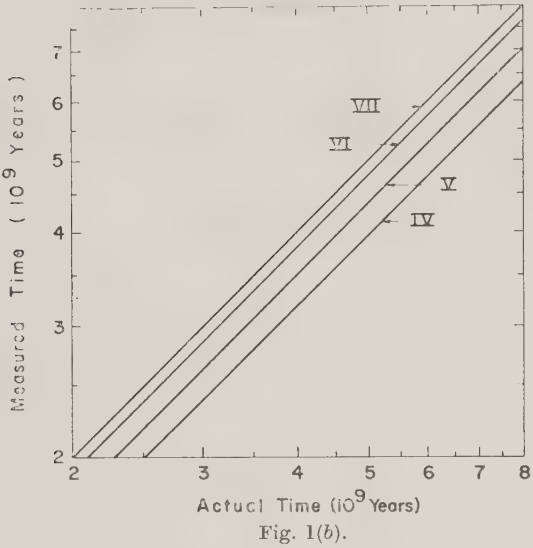

Fig. 1(*b*).

Fig. 1(a) and (b). Systematic errors in the K^{40}–Ar^{40} dating method due to diffusion of argon. The true age is compared with the measured age for several values of the parameter D/a^2, the coefficient for diffusion of argon from the potassium-bearing grains divided by the square of the grain radius. Values of D/a^2 are (in units of sec^{-1}): $2{\cdot}5 \times 10^{-17}$ for curve I, $7{\cdot}5 \times 10^{-18}$ for II, $2{\cdot}5 \times 10^{-18}$ for III, $2{\cdot}5 \times 10^{-19}$ for IV, 1×10^{-19} for V, 1×10^{-20} for VI, and for VII D/a^2 is zero (no diffusion). The decay constant of K^{40} (λ), was taken as $5{\cdot}54 \times 10^{-10}$ $year^{-1}$, corresponding to a half-life of $1{\cdot}25 \times 10^9$ years. In these calculations, D/a^2 was assumed constant throughout the history of the meteorite, so that the given values of this parameter should be regarded as weighted mean values. It is apparent that very large diffusion errors may be introduced by mean diffusion parameters as small as $2{\cdot}5 \times 10^{-18}$ sec^{-1}, for which the *maximum* measurable age is $\sim$1·6 aeons.

uranium and thorium. This separation certainly took place at temperatures above 1250°K, and argon would have been completely lost at the time of this event. The time elapsed since the lead separation took place in the Holbrook chondrite is 4·65 ± 0·07 aeons, according to the determination by Marshall and Hess (1958). In the case of Holbrook we see that it is quite unlikely that the last total expulsion of argon occurred more than 4·78 aeons ago, although argon might have been driven out more recently. The K–Ar date for Holbrook is

$$4{\cdot}40\ {}^{+0{\cdot}09}_{-0{\cdot}11}\ \text{aeons},$$

according to Geiss and Hess (1958). The discrepancy between the true and the apparent argon expulsion dates is therefore not likely to have exceeded 0·5 aeons and we can see from Fig. 1(b) that the average value of D/a^2 in Holbrook probably did not exceed 6×10^{-20} sec^{-1}; it was almost certainly not greater than 10×10^{-20} sec^{-1}. Using a somewhat different approach, we may accept the suggestion (Patterson, 1956; Marshall and Hess, 1958) that all the chondrites form a single array which is actually 4·55 ± 0·07 aeons old.† Then the K–Ar ages of the eight chondrites dated by Wasserburg and Hayden (1955a) and by Geiss and Hess (1958), averaging 4·20 aeons, would mean that these chondrites as a group have been at temperatures consistent with D/a^2 smaller than 5×10^{-20} sec^{-1} throughout the last 4 aeons. These values of D/a^2 are not significantly different; we shall take the value of 5×10^{-20} sec^{-1} to be representative of this group of chondrites. It should be noted that even if one were to choose t as 6·0 aeons, greater than any reported phase separation age, the average value of D/a^2 would be increased to 3×10^{-19} sec^{-1}. As will be shown in the following section, this larger value leads to conclusions very similar to those derived from the smaller value of 5×10^{-29} sec^{-1}.

III. Argon Diffusion Losses as a Function of Temperature

We should now like to consider the maximum temperatures which would be consistent with such low values of D/a^2. Independent values of D and of a are difficult to obtain, since the location of potassium in meteorites is very uncertain. There is far less petrographically-determinable crystalline feldspar in chondrites than expected from the normative mineral composition (Farrington, 1915). At least part of the feldspar constituents may occur as vitreous maskelynite (Roy and Wyant, 1955), for which no values of D or a are available. Fortunately, Geiss and Hess (1958) have performed a series of heating experiments on stone meteorites, measuring rates of argon loss at temperatures between 673°K and 1523°K, from which values of D/a^2 may be calculated; as pointed out above, only this parameter is needed in equation (9), rather than independent values of D and a. Inasmuch as Geiss and Hess employed samples which showed only slight long-term diffusion losses, the fraction f of argon which should have been

† The Pb–Pb dates have been criticised by Hamaguchi, Reed and Turkevich (1957) on the basis of possible contamination with terrestrial lead. If the contaminating lead were close to average crustal lead in isotopic composition, however, the ages determined would not be appreciably in error.

expelled in the time t' during which the meteorite is held at a particular temperature in the heating experiments is given very nearly by the formula for the diffusive loss from a sphere containing an initially uniform concentration of diffusing substance (Boyd, Adamson and Myers, 1947)

$$f = 1 - \sum_{n=1}^{\infty} \frac{6}{n^2\pi^2} \exp\left(-\frac{n^2\pi^2 Dt'}{a^2}\right) \tag{10}$$

This series has been numerically evaluated by Reichenberg (1953). In Table 2 are given values of D/a^2 as a function of temperature, derived from heating experiments by Geiss and Hess on three chondrites and a calcium-poor achondrite.

Table 2. D/a^2 as a function of temperature for stone meteorites*

Meteorite	Temperature (°K)	Fraction of Ar^{40} expelled	Time (hr)	D/a^2 (sec^{-1})
Holbrook	673	0·20	48	$2{\cdot}26 \times 10^{-8}$
Bjurböle	973	0·140	1	$5{\cdot}15 \times 10^{-7}$
Bjurböle	1473	0·942	8	$8{\cdot}30 \times 10^{-6}$
Richardton	973	0·120	1	$3{\cdot}71 \times 10^{-7}$
Norton County	1523	0·925	7	$8{\cdot}42 \times 10^{-6}$

* From heating experiments by Geiss and Hess (1958).

These five points are plotted in Fig. 2(a), and are represented by a straight line whose constants were determined by a least-squares analysis. We note that all the points lie close to this line, despite their derivation from experiments on different meteorites. This fact suggests an identity in the nature and particle-size distribution of the potassium-bearing minerals of the chondrites chosen, and possibly of all chondrites. It is interesting, too, that the point derived from the calcium-poor achondrite, Norton County, fits so well with the data from the chondrites.

Upon extrapolation of the straight line of Fig. 2(a) to lower temperatures (see Fig. 2b), we find that the temperature corresponding to the value of D/a^2 inferred from the Pb–Pb and K–Ar ages is 196°K. The following points should be kept in mind: First, this value of ~196°K is a "mean" temperature in the special sense that short periods above it would have to be counterbalanced by longer periods at lower temperatures because of the exponential relation between D/a^2, t and t^*. Second, it is a maximum value for the long-term "mean" temperature of the meteoritic parent bodies because we have not considered possible diffusion losses during and after the break-up of the parent bodies into individual meteorites. Third, the straight-line extrapolation of Fig. 2(b) may be subject to errors the order of ±30°K, due to uncertainties in the primary data and to the length of the extrapolation. The value ±30°K should cover the error in the line of Fig. 2(b) since there is ample evidence from experiments on other systems that the relationship between log (D/a^2) and T^{-1} is linear over many orders of magnitude (Nachtrieb, 1959).

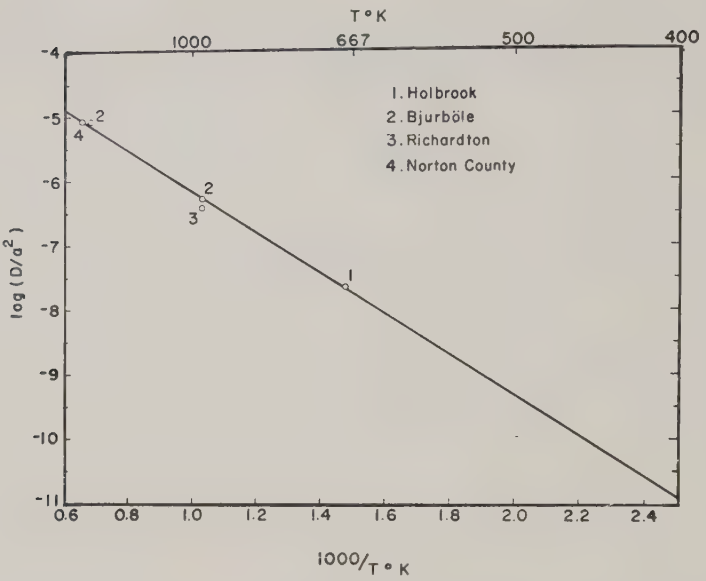

Fig. 2(a). The temperature dependence of D/a^2 for stone meteorites as computed from the heating experiments of Geiss and Hess (1958). The first three meteorites are chondrites, the last (Norton County) an enstatite achondrite. The line fitted to these points by a least-squares analysis obeys the equation: $\log (D/a^2) = -2{\cdot}99 - 319/T$. As discussed in the text, the slope of this line is surprisingly small, indicative of a low activation energy for argon diffusion from the potassium-bearing minerals of these meteorites.

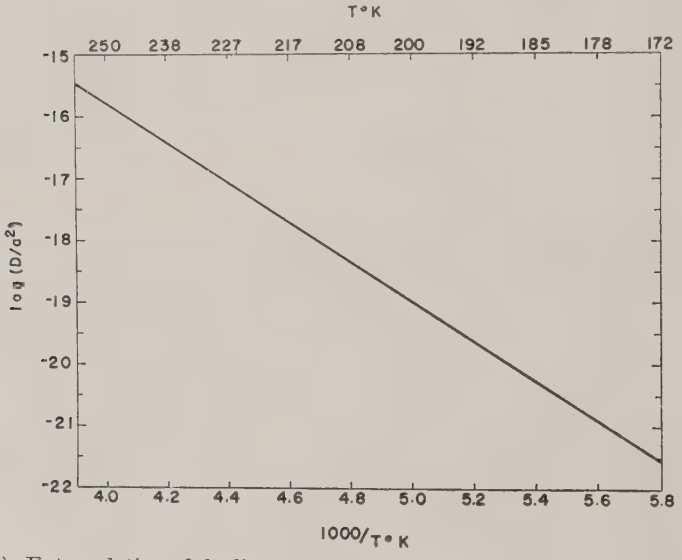

Fig. 2(b). Extrapolation of the line of Fig. 2(a) to lower temperatures. The mean value of D/a^2 for chondrites of $\sim 5 \times 10^{-20}$ sec^{-1} which is derived in the text is seen to imply a mean temperature of 196°K.

We have found that diffusion losses of argon from chondrites are appreciable, over long periods, even at the low temperatures of 196°K. The high rate of diffusion implied by this result may be attributed to both the nature and size of the potassium-bearing grains of the meteorites represented in Fig. 2. The activation energy for the diffusion of argon from these stone meteorites, as calculated from the slope of the D/a^2 plot, is 14 kcal/mole. This value is extremely low compared with that for potassium feldspar (perthitic microline, 23 kcal/mole, Evernden *et al.*, 1959) or glass (potassium–lime–silica glass, 42 kcal/mole, Reynolds, 1956). Apparently the potassium in stone meteorites is located in a mineral distinct from either potassium feldspar or potassium-rich glass. It is important to recall, in this connexion, that crystalline plagioclase loses argon much more readily than does microline (Wasserburg *et al.*, 1956), and the losses should be greater still for glassy plagioclase, i.e. maskelynite. The observed low value of the activation energy is thus in qualitative accord with an assignment of the potassium to plagioclase or maskelynite. Final resolution of this question, however, is contingent upon experimental determinations of the activation energies of argon diffusion from these two minerals.

The conclusions of this section follow from the assumption that argon atoms which diffuse to grain boundaries are then free to escape. Judging from terrestrial evidence, this assumption is certainly valid for samples as small as individual meteorites, although the appropriate grain-boundary diffusion coefficients and characteristic diffusion lengths are not well enough established to test it for objects hundreds of kilometers in radius. Yet the physical situation is not greatly altered (and hence the conclusions remain intact), even if the argon collects in the pores within the silicates rather than escaping. These pores could hardly represent less than one per cent of the volume of the silicates. It would seem that a distribution coefficient of 0·002 to 0·003 is appropriate for the partition of argon between gaseous and silicate phases in meteorites (Gerling and Levskii, 1956; Reynolds, 1959), so that at most ~20 to 30 per cent of the argon would dissolve in the silicate in such a closed system at equilibrium. It is clear that nearly all the argon would have to be lost from each grain before the gas pressure in the pores could retard further diffusion. Then, when the parent bodies were broken up into individual meteorites, the argon in the voids would immediately escape.

IV. The Former Environment of Meteorites

A. *Size and location of the parent bodies*

Temperatures so low as those we have found for chondrites place severe restrictions on the size and orbits of their parent bodies. The aphelia in the orbits of the parent bodies could hardly have extended beyond 5 a.u.†, since otherwise they would have been swept up by Jupiter (Öpik, 1951). As we shall show in the following section, the radiation temperature of a body of meteoritic composition at this maximum distance would be 105°K, assuming its surface characteristics matched those of the moon. We see that heating by long-lived radioactivities could have raised the average interior temperature of a body by no more than

† An astronomical unit (a.u.) is equal to the mean distance from the earth to the sun, $1{\cdot}495 \times 10^8$ km.

196° ± 30° minus 105° or ~60° to 120°K. From Fig. 3, computed from the equations of Allan and Jacobs (1956) on the heating of asteroids, using the most recent chondritic abundances of K, U and Th, we find that this restriction limits the radius of the meteoritic parent bodies to ⩽240 km. Even if the true age were 6·0 aeons ($D/a^2 \cong 3 \times 10^{-19}$ sec^{-1}), the limit on the radius would be raised only to 250 km. Objects closer to the Earth would face higher radiation temperatures, so that a still lower size limitation would have to be placed on an object in a more

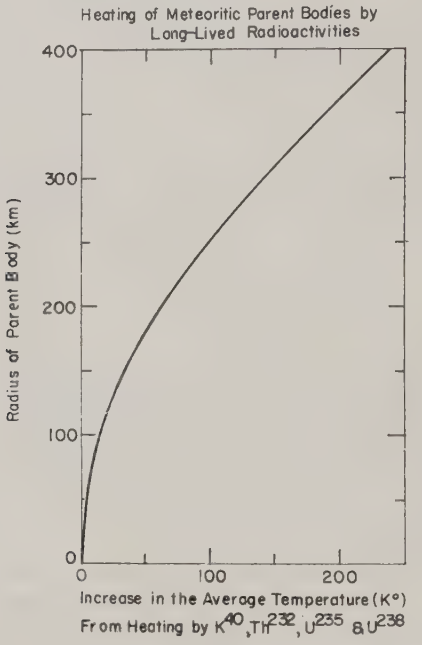

Fig. 3. The increment to the average temperatures of asteroidal sized objects from heating by long-lived radioactivities, 2 aeons after the cessation of strong internal heating by other sources. The initial central temperature was taken as ~1400°K, and the mean thermal conductivity was chosen as ~0·007 cal cm^{-1} °K^{-1} sec^{-1}. The concentrations of K, U and Th assumed were those of Geiss and Hess (1958) and Hamaguchi, Reed and Turkevich (1957); the curve is based principally upon the equations of Allan and Jacobs (1956). In order to obtain the average temperatures from this curve, the given increment must be added to the surface temperature of the object determined by its distance from the sun, as discussed in the text. The curve indicates a rapid increase in the incremental temperature with increasing radius above ~300 km. In order to rationalize the degree of argon retention of the chondrites (average temperature <200°K), their parent bodies could not have been larger than 350 km for any choice of distance from the sun.

nearly terrestrial orbit. The requirement that the radiation temperature *alone* should not exceed 196°K (or, from the larger value of D/a^2, 205°K) implies that the parent body cannot have been in an orbit closer than 1·44 au (1·30 au) to the sun. It would seem from this restriction that the chondrites originated in the region near Mars or beyond, i.e. in the asteroidal belt.

The same sequence of arguments could be used to derive information about the former environment of the achondrites, most of which display lower K–Ar ages than the chondrites. A comparison of the Rb–Sr age of the howardite Pasamonte, 4·54 ± 0·21 aeons (recalculated from the data of Schumacher (1956) using the

Rb^{87} half-life of $4{\cdot}7 \times 10_y^{10}$ measured by FLYNN and GLENDENIN (1959)), with the K–Ar age, $3{\cdot}80 \pm 0{\cdot}23$ aeons, gives an average D/a^2 of 2×10^{-19} sec^{-1}. While it would be necessary to perform heating experiments similar to those of GEISS and HESS on howardites in order to determine D/a^2 as a function of T for this type of meteorite, it seems likely that at least part of the systematic difference between the chondritic K–Ar ages discussed above and those of the achondrites was caused by the consistently warmer environment of the latter. Further discussion of this point will be reserved until we have considered diffusion losses of argon during the "exposure" of individual stone meteorites after break-up of the parent body.

B. *Reheating during the exposure of meteorites*

We have developed the arguments above on the premise that the argon diffusion losses were exclusively due to heating by long- and intermediate-lived radioactivities within the meteoritic parent bodies, after the major processes of meteoritic evolution had ceased. It is well known, however, that the stone meteorites have been exposed as small individuals to cosmic radiation for some tens of millions of years before their collision with the earth. The absence of shielding from cosmic rays implies that they were not larger than a few metres in size. The interiors of such small objects would reach thermal equilibrium with their surfaces on a time scale of days, so that we can be quite certain that their temperatures during exposure were determined only by their surface characteristics and distance from the sun. Since we know that the perihelia of their orbits was at least as close to the sun as 1 a.u., in order for them to collide with the earth, we must consider the possibility that the stone meteorites were strongly enough heated to lose some of their noble gases during exposure.

1. *Radiation temperatures of meteorites in space.* The diffusion losses are very sensitive to temperature, so that we shall discuss in some detail the radiation temperatures to be expected for small objects in orbits about the sun. It has been shown (DRUMMETER and SCHACH, 1958) that the temperature of such an object is related to other physical variables by the equation:

$$T^4 = \frac{C}{R^2} \cdot \frac{B}{S\delta} \cdot \gamma \,(\text{deg } K)^4 \tag{11}$$

where C is the solar constant, R is the distance from the sun in a.u., S is the total surface area of the object, B is its cross-sectional area effective in intercepting solar radiation, δ is the Stefan–Boltzmann constant, and γ is the ratio of solar absorptivity to low-temperature emissivity for the object. Assuming the object to be spherical, and taking C as $1{\cdot}35 \times 10^6$ erg cm^{-2} sec^{-1} (ABETTI, 1957), we find

$$T = \frac{278}{\sqrt{R}} \cdot \sqrt[4]{\gamma} \text{ deg } K \; AU^{1/2} \tag{12}$$

The quantity γ can have a wide range of values, so that, even though it enters as the fourth root, it is important to obtain an accurate estimate of this variable. We know of no measurements on meteoritic surfaces which would enable us to calculate γ, nor is it certain that such a value would apply to meteorites in space,

but we may make use of the lunar sub-surface temperature of 234°K determined by Piddington and Minnett (1949) to estimate γ. Such an estimate rests upon the assumption that the moon's surface is representative of the surfaces exhibited by meteorites and their parent bodies. This assumption is supported by the fact that the albedos of the moon, Mercury, and Ceres are identical within experimental error (Urey, 1952); furthermore, the densities, and presumably the compositions of the moon and the chondrites are very similar (Urey and Craig, 1953; Urey, 1957). We conclude that the lunar γ of 0·502 is characteristic of the stone meteorites and their parent bodies.† With γ determined by the lunar data, the temperature of a spherical object R a.u. distant from the sun is given by

$$T = (234/R^{1/2})\, AU^{1/2} \text{ deg } K \tag{13}$$

it would be somewhat lower for a body of irregular shape. The choice of a temperature as low as 234°K at 1 a.u. is supported by occasional reports of meteorite falls (e.g., Colby, Wisconsin; fell July 4, 1917) which are covered with frost when picked up (Nininger, 1959). The Colby meteorite fractured on impact, according to Nininger, so that its cold interior was exposed at a time when ablation and strong heating of its surface had ceased.

2. *Diffusion losses during exposure.* Now that we have established the relation between the temperature of a meteorite in space and its distance from the sun, we can investigate the effect of argon loss due to solar heating upon the observed K–Ar ages. The exposure ages of stone meteorites are without exception much shorter than the half-life of K^{40}, so that we may treat the limiting case in which argon loss occurs exclusively during exposure as two separate events, first the production of Ar^{40} in the meteorite without loss throughout its lifetime t, and then the loss of a fraction f of the argon content sufficient to give the apparent age t.*

The total argon produced, A, is given by

$$t = \frac{1}{\lambda} \ln \frac{K + A^*/\varepsilon}{K}, \tag{14}$$

and the apparent age corresponding to the retained argon, A^*, is

$$t^* = \frac{1}{\lambda} \ln \frac{K + A^*/\varepsilon}{K} \tag{15}$$

If the resulting age error is called Δ, then

$$\Delta = t - t^* = \frac{1}{\lambda} \ln \frac{K + A/\varepsilon}{K + A^*/\varepsilon} = \frac{1}{\lambda} \ln \frac{Ke^{\lambda t}}{K + A^*/\varepsilon}. \tag{16}$$

Since the fraction of argon lost is

$$f = \frac{A - A^*}{A} = 1 - \frac{\varepsilon K(e^{\lambda t^*} - 1)}{\varepsilon K(e^{\lambda t} - 1)} = \frac{1 - e^{-\lambda \Delta}}{1 - e^{-\lambda t}} \tag{17}$$

† The various classes of stone meteorites differ in their colour, and probably in their intrinsic γ-values as well. We note, however, that radiation damage of the surfaces of the exposed meteorites would be severe in times much shorter than the observed cosmic-ray ages (Ziegler, 1958), so that their surface characteristics during exposure would be closely approximated by those presently exhibited by the moon, even if the lunar surface were initially more highly differentiated than the meteorites.

it follows that

$$\Delta = -\frac{1}{\lambda} \ln [1 - f(1 - e^{-\lambda t})]. \tag{18}$$

Inasmuch as f is not very sensitive to t, we may assume any reasonable value for t, say 4·55 aeons, whence

$$\Delta = -\frac{1}{\lambda} \ln (1 - 0{\cdot}92f) \tag{19}$$

Thus, for example, if f, were 0·9, 0·5, or 0·1, Δ would be respectively 3·2, 1·1, or 0·17 aeons, and would be proportional to f for smaller losses.

The quantity f in equation (19) may now be equated to f in expression (10), and if this is done an expression soluble for the parameter Dt'/a^2 results:

$$\frac{1 - e^{-\lambda\Delta}}{0{\cdot}92} = 1 - \sum_{n=1}^{\infty} \frac{6}{n^2\pi^2} \exp\left(-\frac{n^2\pi^2 Dt'}{a^2}\right) \tag{20}$$

In other words, Dt'/a^2 is a determinable parameter for each meteorite whose K–Ar and solidification age is known, provided we are willing to assume that all the argon diffusion occurred during the cosmic ray exposure era; if we do not make this assumption, then the Dt'/a^2 obtained in this manner is an upper limit.

To determine whether any particular meteoritic orbit, maintained over the exposure era of the meteorite, will admit of a sufficiently low value of Dt'/a^2, it is only necessary to perform a straightforward numerical integration of the orbit. The orbit provides a time interval $\delta t'$ corresponding to each distance interval from the sun, equation (13) gives the temperature at that distance, and Fig. 2b relates this temperature to D/a^2.

Let us take first of all the simplest possible meteoritic orbit—a flight from the Moon to the Earth in a time corresponding to the cosmic ray ages of stone meteorites, 10^7–10^8 years. In this orbit, roughly circular with respect to the sun, D/a^2 would be about 10^{-17}, approximately fifty times larger than indicated by the observed degree of argon retention. The argon retention problem becomes increasingly severe if the meteorites resided for long periods of time somewhat below the surface of the Moon (Urey 1959), unless they were concentrated toward the polar regions.

For the more eccentric orbits, we have found that the numerical integration may be facilitated by the choice of an *effective* t' ($= \tau$) as a small fraction of the cosmic-ray age such that the D/a^2 found by use of expression (20) will be the perihelion value, rather than the mean value over the whole period. This procedure is justified by the observation that diffusion losses during exposure are very sensitive to the perihelion value of D/a^2. We have chosen a sample orbit with perihelion of 1 a.u. and aphelion of 5 a.u., and have calculated D/a^2 as a function of time for one period. We find that the integral of the diffusion function $(D/a^2)\,dt$ may be represented by the perihelion value of D/a^2 for 0·025 of the period, with no diffusion during the rest of the time. Since D/a^2 at 2 a.u. is less than 10^{-5} of the perihelion D/a^2, it is unlikely that any but the most eccentric orbits (aphelion more than ~10 a.u. from the Sun) would lower τ significantly, although orbits with aphelia inside 5 a.u. would have $\tau > 0{\cdot}025$. Accordingly, we shall assume a τ of 0·025 of the cosmic-ray age to be typical of meteorites during their exposure,

so that we may interpret D/a^2 in expression (10) as the perihelion value. The choice of this value of τ will therefore lead to an underestimate of diffusion losses for orbits with perihelion distances much less than 1 a.u. or with aphelia less than 5 a.u. from the Sun.

We may now estimate the importance of argon diffusion losses during exposure. Eberhardt and Hess (1959) have reported cosmic-ray ages for five of the eight chondrites whose K–Ar ages were discussed above; the average of their He^3 ages for these meteorites is ~24 million years. Let us take as an "average" chondrite of this group one which spent $2{\cdot}4 \times 10^7$ years ($\tau = 6 \times 10^5$ years) in an orbit with perihelion of 0·95 a.u., such that the perihelion temperature was 240°K. From Fig. 2(b), the appropriate D/a^2 is $5{\cdot}0 \times 10^{-17}$ sec^{-1}; f is found to be 0·101, and $\Delta = 0{\cdot}16$ aeons. Even if no argon loss had taken place in the parent body of such an "average" meteorite, its measured age would be 4·39 aeons, rather than the true age of 4·55 aeons!

This being the case, we may be reasonably certain that meteorites with K–Ar ages in the vicinity of 4·4 aeons followed highly eccentric orbits in flight, with aphelia at least 4–5 a.u. from the sun (and perihelia not much less than 1 a.u. from the sun), in other words, we may be quite confident that these meteorites came from the asteroidal belt.

V. Discussion

A. *Origin of the diffusion losses*

If we could distinguish the effects of the two periods of diffusion losses (in the parent bodies and during exposure), it would be possible to gain more detailed information about each. In principle, this can be done, given reliable K–Ar and cosmic-ray ages for a large number of meteorites of the various classes, and data to establish the relationship between D/a^2 and T for each class. Strong heating in the parent bodies would manifest itself in systematically low K–Ar ages, not correlated with cosmic-ray ages, among those classes of stone meteorites affected. Such trends of systematically low ages have been observed for the shergottites (Shergotty, 0·56 aeons, Geiss, 1957; Padvarninkai, 1·0 aeon, Gerling and Levskii, 1956), the crystalline chondrites (Gerling and Rik, 1955), and, to a lesser extent, for the howardites and eucrites (Geiss and Hess, 1958). In order to rationalize these trends as due principally to losses during exposure, it would be necessary to postulate that each class of meteorites had been placed in a single orbit, or a group of closely similar orbits, during the break-up of the parent bodies. If this were the case, a highly selective dispersal mechanism, sensitive to the location of the meteorite in the parent body, must be postulated for the break-up. It is much more likely that the major trends in the K–Ar ages were established in the parent bodies, rather than during exposure. In that case, the data support the model of a forthcoming paper of this series (Fish *et al.*, 1960), according to which the achondrites originated in deeper, and therefore warmer, regions of their parent bodies than did the chondrites.

It should be noted, however, that it is by no means impossible that at least some of the low K–Ar ages cited were due to diffusion losses during exposure. Even in the extreme case of the shergottites, all the Ar^{40} losses could have occurred

during exposure if the perihelia of their orbits had been at 0·55 a u. for Shergotty and 0·63 a.u. for Padvarninkai, taking their respective cosmic-ray ages to be 5×10^6 years (He^3; Eberhardt and Hess, 1959) and 2×10^7 years (Ar^{38}; Gerling and Levskii, 1956), and assuming that they follow the same D/a^2 vs. T relation as do the chondrites.† In fact, there is some independent evidence that diffusion losses during exposure were important for Shergotty at least: the Ar^{38} cosmic-ray age for this meteorite is more than twice the He^3 age (Eberhardt and Hess, 1959). While Eberhardt and Hess have suggested that this is due to an anomalously high production rate of Ar^{38} in this calcium-rich achondrite, it may also be interpreted as an indication that both spallation products were lost by diffusion during exposure, the helium more rapidly than the argon. If this were the case, both determinations of the cosmic-ray age for Shergotty would be subject to large negative systematic errors. Clearly, diffusion losses during exposure should have contributed to the very large Δ for the shergottites, although the arguments presented above indicate that the major argon losses should be assigned to heating in the parent bodies.

B. *Diffusion losses of other noble gases*

The discussion of the shergottite ages serves to demonstrate the importance of the diffusion of noble gases other than Ar^{40} from stone meteorites. In the course of their heating experiments, Geiss and Hess (1958) were able to secure information on the rate of diffusion loss of Ar^{38} from stone meteorites; they observed that the fraction of Ar^{38} expelled was less than half that of Ar^{40} over a wide range of conditions. This result is easily understood, since losses of the spallation product, Ar^{38}, from the sites within the silicate crystals and metal grains where it is produced, would be much more difficult than the loss of Ar^{40} from maskelynite or feldspar. Nevertheless, the fraction of Ar^{40} lost from Shergotty, calculated under the assumption that the true age is 4·55 aeons, is 0·968. As much as one-half of the Ar^{38} and Ne^{21}, and probably more of the He^3 produced by cosmic radiation, could have been lost under these extreme conditions. Apparently, the reported cosmic-ray ages for stone meteorites may in some cases be too low by factors of 2 or greater, and errors the order of from 10 to 20 per cent due to diffusion losses should be quite common.

Another dating method that is affected by diffusion losses is the I^{129}–Xe^{129} measure of the time between nucleogenesis and the retention of xenon in the meteorites. This method has been applied, thus far, to three meteorites: Beardsley (Wasserburg and Hayden, 1955b), Nuevo Laredo (Reynolds and Lipson, 1957) and Richardton (Reynolds, 1960). In these cases only minute amounts of xenon, of atmospheric composition, were found, giving ages of 0·41 aeons and 0·47 aeons,

† The potassium in the shergottites certainly resides in maskelynite, which is one of their principal constituents. If our argument that the potassium in chondrites is present in grains of plagioclase or maskelynite is correct, we would expect the log (D/a^2) vs. T^{-1} curve for the shergottites to have the same or an even less steep slope, but possibly a different intercept, as that of Fig. 2. We also note that these perihelion distances were calculated using expressions (14) and (10), with $\tau = 0{\cdot}025$ of the cosmic-ray age; this value for τ may be somewhat too large for an orbit with perihelion as small as 0·6 a.u. Correction for this effect would tend to increase the perihelion distances given, as would consideration of possible negative errors in the reported cosmic-ray ages. Clearly, diffusion losses can be quite severe for orbits which are well within the realm of plausibility.

respectively.† These ages have often been interpreted as the time between nucleogenesis and the formation of the meteorites in question, but they probably indicate the time required for the cooling of the parent bodies of these meteorites to temperatures at which diffusion losses are negligible.

In the first two cases, no anomalous component of Xe^{129} was observed, so that the time T between nucleogenesis and the retention of xenon was computed to be $\geqslant 0{\cdot}41$ and $\geqslant 0{\cdot}47$ aeons, respectively. In the third case excess Xe^{129} was found in sufficient abundance to fix T as $\leqslant 0{\cdot}32$ aeons. For convenience let us divide the time T into $T_1 + T_2$, with T_1 denoting the time elapsed between the last nucleogenetic event and the formation and internal heating of the meteoritic parent bodies, and T_2 the time required for the parent bodies to cool to temperatures at which xenon diffusion losses are negligible. Without information on the xenon diffusion rates for these stones, it is not possible to say whether xenon would begin to be retained at ~400°K or whether it would continue to be lost until the parent body had cooled to ~200°K as might be the case if I^{129} is concentrated at grain boundaries (Urey, 1955). In spite of this uncertainty, the important point to note is that T for Richardton is approximately equal to the value of T_2 obtained on the assumption that the meteoritic parent body was only 250 km in size, and would be an order of magnitude too small for bodies only 500 km in radius. This observation establishes first that the diffusion of xenon greatly alters the results of the I-Xe dating method, and makes the time T_1 between the last event of nucleogenesis and the formation of the meteoritic parent objects virtually inaccessible by the I–Xe method. It also provides the first direct evidence that the bodies in which the meteorites were *synthesized*, as well as the bodies in which they resided for 4–4·5 aeons, were no larger than asteroids. This observation provides justification for the development of a theory which accounts for the synthesis of meteorites entirely within asteroidal-sized objects (Fish, Goles, and Anders, 1960).

C. *The properties of the parent bodies of the meteorites*

We have set an upper limit to the size of the parent bodies of the chondrites; from this maximum radius ($\leqslant 250$ km), we may infer the maximum pressure in their interiors, and making use of the calculations of Allan and Jacobs (1956), may estimate their minimum cooling times. These properties, when compared with those which have been proposed for the parent bodies of other classes of meteorites, delineate a number of serious problems in understanding the meteorite evidence, and suggest several crucial experiments which might resolve these difficulties.

Diamonds have been observed in ureilities and some octahedrites; the pressure required for the production of diamond via the graphite–diamond transition is $\sim 3 \times 10^4$ atm (Urey, 1957). The maximum pressure in the interior of an object of chondritic density and 250 km in radius is 940 atm, so that, if the diamonds in the ureilites and octahedrites were formed from graphite as a stable product, these meteorites must have evolved deep within objects much larger than the parent bodies of the chondrites. In order to avoid postulating parent bodies

† In the papers cited, the authors note that all the xenon examined could have been due to atmospheric contamination, so that there is no evidence that these meteorites have retained *any* xenon, primaeval or radiogenic.

of several markedly differing sizes, an alternative suggestion should be considered. If these diamonds had been formed as a metastable phase in the decomposition of cohenite, pressures in excess of 10^4 atm would not be necessary, and the diamond-bearing meteorites could have evolved in the same asteroidal-sized objects as gave rise to the chondrites. This possibility will be discussed in detail in a future paper of this series. Determinations of K–Ar and cosmic-ray ages of ureilites, coupled with heating experiments to establish the D/a^2 vs. T relation for diffusion losses of their noble gases, would be most useful in fixing limits on the size of their parent bodies and thereby give evidence on the mode of production of their diamonds.

In order to obtain information on the properties of the parent bodies of the octahedrites, we might consider the time required for them to cool to temperatures of the kamacite–taenite transformation region. Asteroids of a few hundred kilometres in radius (with "normal" concentrations of U, Th and K), once melted at their centres, would cool to 600°–800°K in times the order of several hundred million years (Allan and Jacobs, 1956; see especially Figs. 9 and 10 of their paper). A time span of this magnitude would explain the absence of excess Xe^{129} in Beardsley and Nuevo Laredo; it is also concordant with the cooling time proposed for the objects in which the Widmanstätten patterns of the octahedrites were formed (Uhlig, 1954; Urey, 1956, 1957). This would imply that the parent bodies of the chondrites and the octahedrites were similar, although the available pressures in asteroidal-sized objects, as pointed out by Allan and Jacobs, are two orders of magnitude less than those postulated by Uhlig, while objects large enough to give Uhlig's pressures, i.e. of lunar size, would heat up rather than cool. If the octahedrites were produced in asteroidal-sized bodies, then Urey's model, or some less stringent scheme for the formation of the Widmanstätten patterns would be applicable.

Independent evidence on the size of the parent bodies of the octahedrites might be obtained by determining K–Ar and cosmic-ray ages, and D/a^2 as a function of T for the silicate inclusions occasionally found in iron meteorites. Such inclusions, however, are generally poor in potassium and would be difficult to date satisfactorily. One might also study the silicates of the stony-irons, since some meteorites of this class display octahedral structure in their metallic portions (e.g. Brenham, Estherville). A K–Ar age of 3·5 aeons has been reported for Brenham (Thomson and Mayne, 1955); an age so great suggests that the parent body of this meteorite cannot have been much larger than those of the chondrites. Geiss and Hess (1958) have given a detailed criticism of this determination, however, concluding that it may be subject to serious errors. Lovering, in two recent papers (1957a,b), has proposed that the typical parent body of the irons and pallasites was of lunar size, but his arguments have been criticized by Urey (1958; see also Lovering, 1958). We note also that Lovering has not resolved the apparent contradiction between the requirement that the interior of this parent body should cool to 600°–800°K (in order to form the Widmanstätten patterns), and the calculations of Allan and Jacobs cited above. In the absence of more experimental data, the size of the parent bodies of the pallasites may be considered an open question.

While we have insufficient data to set limits upon the size of the parent bodies of the pallasites or of the iron meteorites, we note that evidence has recently been

presented for the existence of iron cores in the parent bodies of the stone meteorites. In two papers of great significance, Stacey and Lovering (1959) and Lovering (1959) have shown that two chondrites and a calcium-rich achondrite possess substantial preterrestrial magnetic moments, which they interpreted as due to the magnetic fields of their parent bodies. These magnetic fields, in analogy with that of the earth, were probably caused by convection in a fluid conductive core, most likely of iron–nickel. Although we have no direct evidence that the chondrites studied, Homestead and Mount Browne, which have not been dated by the K–Ar method, originated in asteroidal-sized bodies, we note that the discussions of the formation of an iron core and of convection in the core of such an object given by Fish *et al.* (1960) demonstrate the feasibility of a convective iron core in bodies of a few hundred kilometres or less in radius. Also, the K–Ar age of the achondrite studied, Moore County (3·23 aeons, Geiss and Hess, 1958), and its cosmic-ray age (10 million years, Geiss, 1957), imply that its parent body was of asteroidal size. If the presumably small parent bodies of these meteorites had iron cores, then at least some of the iron meteorites may be fragments of these cores.

We have seen that a study of the effects of diffusion of noble gases from meteorites can provide valuable information about the former environment of the meteorites, both while in their parent bodies, and during exposure. Data on diffusion losses of radiogenic He^4 might be exceptionally informative, since this gas diffuses more rapidly than argon under similar conditions, so that its retention in meteorites is a more sensitive indicator of temperature. Although we have concentrated our attention upon the chondrites, the same method could be applied to other classes of meteorites, once appropriate data become available. Much information concerning the origin of the meteorites may be obtained in this manner, and we trust that the necessary experiments will soon be undertaken.

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Studies in biogeochemistry—I

A biogeochemical periodic table. The data

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Abstract—Information of interest in biology, geology and chemistry has been collected from the literature and summarized in a biogeochemical periodic table. Available data on abundance, geochemical character, nutritional importance, electronegativity, complexing tendency, oxidation state, covalent and/or ionic radius, ionic potential and ionization potential are reported for each element.

Introduction

The basic problem of understanding organisms in their natural habitats involves essentially every scientific field. Certain aspects of this general problem are the immediate concern of physicists, chemists, biologists and geologists. Other more or less detailed features are of prime consideration in the work of geochemists, pedologists, nutritionists, agricultural researchers, enzymologists, biochemists and other scientific investigators. Researchers in many of these areas are currently examining the "fine structure" of the problem germane to their particular disciplines. Although these detailed investigations are of utmost importance, a broader view perhaps may reveal some useful generalizations. It is also of interest to note that there are several concepts and supporting numerical data that have enjoyed wide applicability in many different areas. Consequently, the purposes of this paper are: (i) to summarize and collect data useful in a variety of fields, and (ii) to present such data in an abbreviated form so that general trends and relationships of broad significance may become apparent. To this end it seemed best to view the data against the framework of the long form periodic table.

Biogeochemistry

The term "biogeochemistry" was first employed by Vernadsky who described the field as follows (Vernadsky, 1939)†: "Biogeochemistry, which is a part of geochemistry and has peculiar methods and peculiar problems of its own, may be finally reduced to a precise quantitative mathematical expression of. . .living nature in its indissoluble connexion with the external medium. . . . Hence it seems to me that in the phenomena of life we may approach in a new way a number of fundamental problems . . . , on one hand, and on the other relate the biological phenomena with the branches of science dealing with atoms. . . ."

A large amount of biogeochemical research has been done by Vernadsky's school in the Soviet Union. Vinogradov (1943) has presented a brief discussion of these activities. Hutchinson (1943, 1950, 1954), in the United States, has been

† See references to "Studies in Biogeochemistry—II" p. 208.

quite active in the field; and a "Survey of existing knowledge of biogeochemistry" has been begun (KAMEN, 1946; BERTRAND, 1950; HUTCHINSON, 1950; VINOGRADOV, 1953). POLANSKI (1949), in Poland, has published at least one paper; and WARREN *et al.* (1955) in Canada have made many contributions to biogeochemical prospecting. HAWKES (1957) has presented a useful review of the principles involved in this new method of locating ore bodies. Other recent publications in this area include biogeochemical studies of the rare earths (ROBINSON *et al.*, 1958) and of copper–tin mineralization in south-west England (MILLMAN, 1957).

In attempting to collect and condense qualitative, semiquantitative and quantitative data of interest in biology, geology and chemistry, the problem of selection is ever present. The procedures adopted here are based on the following considerations.

ABUNDANCES†

In any study of organisms and their environments from a biogeochemical point of view, elementary composition is clearly an important variable. Environments are considered initially.

Since the earth was formed by some process of condensation or accretion of cosmic matter (SUESS and UREY, 1956), cosmic abundance must have played an important role in determining the chemical composition of the primordial planet. In the course of time, however, geochemical and physical processes effected many changes. A core, a mantle and a crust were formed. Volcanoes discharged gases into the primal atmosphere. Great oceans appeared and rivers leached the crust of the earth and brought salts to the seas. Then, somehow, life arose, most probably in the seas, and organisms came into being. Thus three kinds of abundances: cosmic, crustal and oceanic, must all have been directly or indirectly involved in determining the elementary composition of organisms.

Cosmic abundance

SUESS and UREY (1956) have published values for the relative elemental abundances in the universe. These abundances are reported in atoms of the particular element per a fixed number of silicon atoms. Since some of these values and other abundance data are probably good at best to one significant figure and differ greatly in magnitude it will prove convenient to use a logarithmic scale. Thus, in analogy to the pH scale, a pA scale will be employed, where:

$$\mathrm{p}A^* = -\log A^*$$

and A^* is the relative cosmic abundance expressed in atoms per 10^4 atoms of silicon. On this scale, pA^* values less than zero correspond to relatively high abundance, p$A^* = 0$ (e.g. Li) indicates an A^* of 1 atom/10^4 Si atoms. Increasing positive values of pA^* are related to decreasing abundance.

Crustal abundance

A table of the average amounts of the elements in crustal rocks is available in the excellent book by MASON (1958). His data, reported in parts per million, have

† Since this paper was submitted for publication a very useful paper of general interest has appeared (GREEN, 1959).

been converted to gramme-atoms per kilogram and negative logarithms of these quantities employed.

Oceanic abundance†

Vinogradov (1953) has presented data on the elementary composition of sea-water in per cent (chlorine = 19·00). Similar data and references are available in Harvey's (1955) fine book and elsewhere (Svedrup *et al.*, 1942). Vinogradov's data were converted to gramme-atoms per kilogram and pA values calculated.

For the major elements in sea-water, these pA values are probably better than the two significant figures reported. For the minor constituents, however, pA values may be good only to $\pm 1{\cdot}0$ or even $\pm 2{\cdot}0$. Although progress has been made in elucidating the factors controlling rare metal concentration in the seas (Krauskopf, 1956), our knowledge of the oceanic abundance of many of these elements is indeed meagre (Richards, 1956).

Location of cosmic, crustal and oceanic abundance in table

In the biogeochemical periodic table (Fig. 1) negative logarithms of the various abundances have been placed in the parentheses just to the right of the element's symbol. These pA's are arranged from bottom to top according to their probable geochemical chronology, i.e. cosmic, pA* (bottom); crustal, pA (middle); and oceanic, pA (top). As previously indicated A* is in units of atoms/10^4 Si atoms, and the A's are expressed in gramme-atoms per kilogram. If an element occurs in nature in minute amounts or has not been detected but has been synthesized the symbol "syn" appears in the parentheses commonly reserved for oceanic abundance.

Biospheric abundance

From the elements dissolved in the sea ordered structures evolved. Amino acids, proteins, enzymes and organisms were formed. The composition of primitive organisms was naturally profoundly influenced by the composition of the ancient seas in which they dwelt. In fact, the most primitive modern invertebrates that live in the present ocean have tissue fluids the composition of which hardly differs from the composition of sea-water (Vinogradov, 1953, p. 569). With evolution, however, the average composition of living matter—the biospheric abundance—became more complex.

In collecting the data for a semiquantitative classification, the pioneering work of Webb and Fearon (1937) and Webb (1937) has been used as the primary source, although Hutchinson's (1943) classic paper was also employed and information from the book by Underwood (1956) was likewise considered. Vinogradov's (1953) work was, of course, consulted. The books by Mason (1958), and by Rankama and Sahama (1950) provided literature references and helpful discussions.

The following scale was adopted for use in the table (percentages are from Webb and Fearon (1937):

† Two additional excellent references are now available (Richards, 1957; Sears, 1959).

THE BIOGEOCHEMICAL PERIODIC TABLE

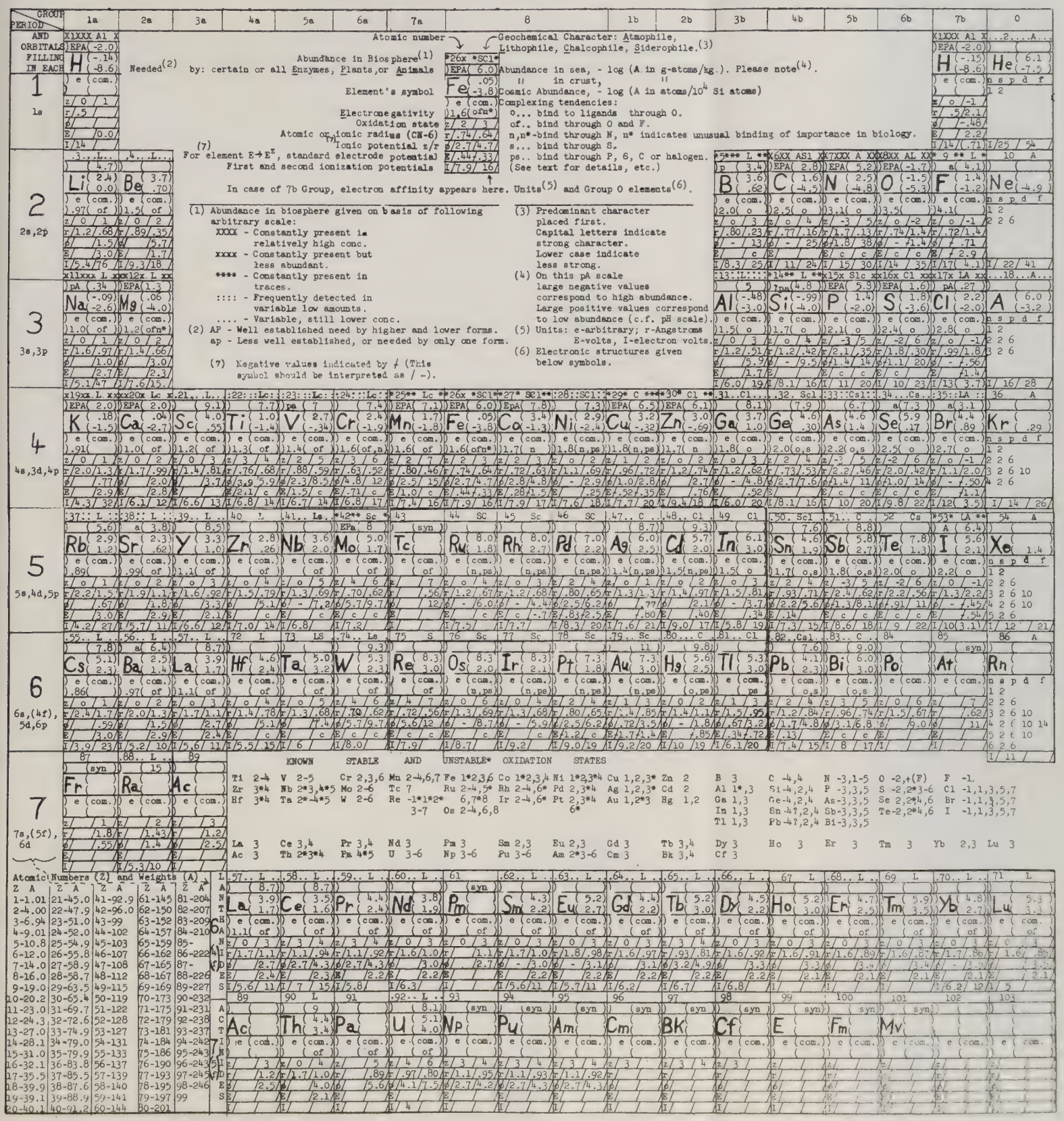

GROUP / PERIOD
1a 2a 3a 4a 5a 6a 7a 8 1b 2b 3b 4b 5b 6b 7b 0
Atomic number
Geochemical Character: Atmophile, Lithophile, Chalcophile, Siderophile.(3)
Abundance in Biosphere(1)
Abundance in sea, - log (A in g-atoms/kg.). Please note(4).
Needed(2) by: certain or all Enzymes, Plants, or Animals
in crust,
Element's symbol
Cosmic Abundance, - log (A in atoms/10^4 Si atoms)
Electronegativity
Complexing tendencies:
Oxidation state
Atomic or ionic radius (CN-6)
Ionic potential z/r
For element E→E^z, standard electrode potential
First and second ionization potentials
In case of 7b Group, electron affinity appears here. Units(5) and Group O elements(6).
(1) Abundance in biosphere given on basis of following arbitrary scale:
XXXX - Constantly present in relatively high conc.
xxxx - Constantly present but less abundant.
**** - Constantly present in traces.
:::: - Frequently detected in variable low amounts.
.... - Variable, still lower conc.
(2) AP - Well established need by higher and lower forms.
ap - Less well established, or needed by only one form.
(3) Predominant character placed first.
Capital letters indicate strong character.
Lower case indicate less strong.
(4) On this pA scale large negative values correspond to high abundance. Large positive values correspond to low abundance (c.f. pH scale).
(5) Units: e-arbitrary; r-Angstroms E-volts, I-electron volts.
(6) Electronic structures given below symbols.
(7) Negative values indicated by / (This symbol should be interpreted as / -).
KNOWN STABLE AND UNSTABLE* OXIDATION STATES
Atomic Numbers (Z) and Weights (A)

Fig. 1.

XXXXXX: these elements are constantly present in the tissues and fluids of plants and animals. They occur in relatively high concentrations (approximately 1–60) per cent.

xxxxxxxxx: these elements are also constantly present but are less abundant (approx. 0·05–1) per cent.

*********: constantly present in trace amounts (less than 0·05) per cent.

::::::::::::::: frequently or occasionally present in variable (usually low) concentrations.

.....: have been detected in organisms in variable still lower concentrations.

These symbols—the biospheric abundance code—are placed in the top rectangular frame above the element's chemical symbol. The atomic number (left side of rectangle) and the geochemical character (right side) are also included. Geochemical character is discussed in the next section. If no abundance code is included, the element has not, as yet, been detected in living tissue (e.g. Ru, Rh and Pd) or no data concerning the element's occurrence in the biosphere were available to the writer.

Since various sources present conflicting data, assignment of the biospheric abundance code involves, in many instances, arbitrary selection. It must also be emphasized that the classification is certainly not rigid (especially for the minor elements) and when new data accumulates (. . .) elements may be classed as (: : :) or (***).

Geochemical Character

Goldschmidt (1954) has classified the elements according to their tendency to occur in various geochemical phases. Elements that are found in the iron phase (and presumably in the iron core of the earth) are called **S***iderophile* elements. Those occurring in the silicate phase are termed **L***ithophile*, and those that are found in sulphide ore—**C***halcophile*. The **A***tmophile* elements exist in the atmosphere as volatile elemental or compound gases.

The geochemical character of each element is given in the right-hand side of the rectangular space above the element's symbol. If an element is strongly chalcophile, a *C* is placed in this space. Weaker chalcophiles are designated by *c*. Analogous symbolism is used for the other types of geochemical character. If an element has a mixed character, the predominant character is placed first.

Enzymes, Plants and Animals

As the organisms evolved, semipermeable membranes, closed circulatory systems, and mechanisms for concentrating needed elements for specialized functions appeared. Highly-diversified activities became possible as the result of complex metabolic patterns and specialized morphology. The animals and plants conquered the land (Pearse, 1950).

An indication of the essentialness of a particular element in the proper functioning of enzymes, plants, and animals is provided in the)space(directly above the element's symbol.

Enzymes

If the element is known to be essential to one or more enzymes an *E* is placed in the left of the)space(. The classification is based on material from several sources (Neilands and Stumpf, 1958; Williams, 1953; Crook, 1958; and Green, 1941).

Plants

If an element is required by higher and lower plants, a *P* is placed in the)space(. If it is required by either higher or lower plants or if its essentiality has not been conclusively established, the symbol *p* is inserted. This classification is based on discussions by Arnon (1958), and Mehlich and Drake (1955). Stiles (1946) was also consulted.

Animals

An analogous symbolism was employed to describe results of experiments in animal nutrition. Several excellent books are available (Lamb *et al.*, 1958; Gilbert, 1957; Underwood, 1956; Monier–Williams, 1949; Maynard and Loosli, 1956; Bear, 1955; Stiles, 1946; and Stohl, 1939). Two important reviews (Bear, 1958; and Todd, 1959), were also studied.

Chemical Properties

Nuclear properties such as binding energy, half-life and cross-section (Suess and Urey, 1956) undoubtedly are of prime importance in determining the cosmic abundance of the elements, but properties that depend on the extranuclear atomic structure largely determine the biogeochemical fate of the elements. Thus, after the earth was formed, the geochemical redistributions that took place were dependent on physicochemical properties such as density, thermodynamic stability, crystal structure, etc. In the case of the hydrosphere and biosphere solubility is of particular importance.

For an evolving organism the selection of an element for a particular need will be governed by "availability" and an appropriate chemistry. Although availability and abundance are related they are certainly not identical. Organisms with concentrator mechanisms have increased the availability of certain elements for use in their metabolic processes despite the fact that the abundance of these elements in the external medium is essentially fixed. The twin criteria of availability and appropriate chemistry provide an important basis for understanding many features of the biochemistry of evolution.

Electronic configuration

Electronic configuration plays a major role in determining the chemical properties of the elements. The long form periodic table is an arrangement based on electronic configuration. Unfortunately space in the table did not permit inclusion of detailed configurations for all the elements, but a reasonably satisfactory method for presenting most of this information was developed. Detailed configurations for all of the inert gases have been included. Values for the principal quantum number, *n*, are presented in the first column directly under the element's symbol.

Figures in the next column represent the number of s electrons with a principal quantum number given by the n value in the first column. Numbers of electrons in the p, d, and f orbitals are listed in successive columns. For example the rare gas xenon contains: two $1s$ electrons, two $2s$, six $2p$, two $3s$, six $3p$, ten $3d$, etc. For each period the orbitals that are filling and *the order in which they fill* are indicated on the left side of the table.

The determination of approximate configurations from the table using the information described in the preceeding paragraph is illustrated with a particular example, the cobalt atom. The electronic structure of A is $1s^2$, $2s^2$, $2p^6$, $3s^2$, $3p^6$ (numbers preceding the letters are n values, superscripts designate numbers of electrons). Kr has the configuration: ($1s^2$, $2s^2$, $2p^6$, $3s^2$, $3p^6$), $3d^{10}$, $4s^2$, $4p^6$. In comparing these two configurations it becomes apparent that ten electrons have entered the $3d$ orbital; two electrons, the $4s$; and six electrons, the $4p$ in the course of completing period 4. For this period the filling order is: $4s$, $3d$, $4p$. Combining this information with the electronic structures for A and Kr makes it clear that the electronic structure for Ca must be: $1s^2$, $2s^2$, $2p^6$, $3s^2$, $3p^6$, $4s^2$. For cobalt (atomic number 27): $1s^2$, $2s^2$, $2p^6$, $3s^2$, $3p^6$, $3d^7$, $4s^2$ would be expected. In general, configurations determined in this manner are essentially correct; but, because of the close spacing of some of the levels, exceptions are encountered. In period 4, Cr and Cu have one more electron in the $3d$ orbital and one less in the $4s$ than would be anticipated. In period 5, Nb, Mo, Tc, Ru, Rh and Ag have one more electron in $4d$ and one less less in $5s$ than would be predicted. Pd has no $5s$ electrons and ten $4d$ electrons. In period 6 with the exception of La and Gd, the lanthanides behave in a regular manner. Ir has nine $3d$ electrons and no $6s$. Pt and Au have one less $6s$ and one more $5d$ than would be anticipated. In period 7 with the exception of Th, the actinides are well behaved except that one electron regularly appears in the $6d$ orbital. Detailed tables of electronic configurations are available (Moeller, 1952).

Atomic number, Z, *and atomic weight*, A

The atomic number appears in the long rectangular space two spaces above the element's symbol. Corresponding atomic weights (to three significant figures) can be readily obtained by consulting the table in the lower left corner of Fig. 1.

Electronegativity

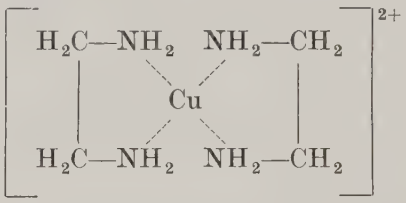
Pauling (1940) has defined electronegativity as "the power of an atom in a molecule to attract electrons to itself". This same author has devised an electronegativity scale on bond strengths. Pritchard and Skinner (1955) have reviewed the applications and misapplications of this concept in chemistry and recently Allred and Rochow (1958) have compiled an extensive list of electronegativity values based on an electrostatic approach. Sanderson (1958), in the light of his earlier work on the subject, has discussed the Allred–Rochow treatment. Allred and Rochow's values have been listed in Fig. 1 directly below the elements' symbol in the e space. Of the elements with reported electronegativities, fluorine ($e = 4{\cdot}1$) is the most electronegative and caesium ($e = 0{\cdot}86$) is the least. The original values are reported to three significant figures but for compactness the data in Fig. 1 are reported to only two.

In chemistry electronegativities have been used to estimate the ionic character of chemical bonds and for other purposes (Pritchard and Skinner, 1955; Moeller, 1952). Highly-electronegative elements will be expected to form anions, and elements with low electronegativities will exist in nature as cations. As a

rough rule, if the electronegativity difference between two elements is equal to or greater than 2·1 units, the bond formed between atoms of these elements will be 50 per cent or greater than 50 per cent ionic. Ringwood (1955a) has discussed the importance of electronegativity in geochemistry and has observed that: "Whenever diadochy in a crystal is possible between two elements possessing appreciably different electronegativities the element with the lower electronegativity will be preferentially incorporated because it forms a stronger more ionic bond than the other".

Co-ordination tendencies

A substance composed of a central atom or ion (usually a metal) surrounded by electron donors (ligands) is called a complex or co-ordination compound. Ligands may be atoms, ions or molecules. If the ligands contain two or more electron-releasing centres so that combination with the central atom or ion results in a structure containing one or more rings the co-ordination compound is called a chelate. The familiar copper-II tetrammine ion, $[Cu(NH_3)_4]^{2+}$, is a typical complex ion. The bis(ethylenediamine) copper-II ion:



contains two chelate rings. The ligand, ethylenediamine, has two electron-releasing centres (the NH_2 groups) attached to the metal ion. Such a ligand is said to be bidentate (two teeth). Polydentate ligands are well known. Bailar (1956) has classified the elements according to the types of atoms with which they seem to co-ordinate most firmly. The classification is qualitative and is not intended to be rigid. The types merge with one another. In Fig. 1 complexing tendencies are presented under the heading "com". The following symbolism is employed:

o: Primarily bind to ligands through oxygen.

of: Most bind to ligands through oxygen. Fluorine complexes are also common. Tendency to complex with other non-metals becomes more pronounced with increasing group number.

n: Primarily bind to ligands through nitrogen.

n:* This symbol used for iron and magnesium. These biologically-important elements generally bind to ligands through oxygen. In porphyrins and phthalocyanins the ligand frequently "forces" unusual chelation through N. The magnesium in chlorophyll and the iron in haemin are found co-ordinated to four N atoms in a square planar arrangement (Bailar, 1956, p. 74).

s: Bind to ligands through sulphur.

ps: Bind to ligands through phosphorus, sulphur, halogen or carbon. The tendency to complex with other non-metals and lighter halogens increases with decreasing group and period number.

The stability of complexes depends on the nature of the ligand and the nature of the metal. For co-ordination compounds formed by certain cations, however, it has been found possible to establish a stability sequence (Mellor and Maley, 1948; Irving and Williams, 1953; Williams, 1953; Williams, 1959) that is independent of the nature of the ligand. This so-called "natural order", a sequence of very general validity, is: $Mn^{II} < Fe^{II} < Co^{II} < Ni^{II} < Cu^{II} > Zn^{II}$. With a given ligand this sequence implies that the Cu^{II} complex will be most stable and the Mn^{II} complex least stable. The other complexes will be of intermediate stability. A tentative extension of the above sequence has been suggested by Basolo and Pearson (1958) such that for divalent cations of the following metals:

$$Pt > Pd > Hg > (UO_2) > Be > Cu > Ni > Co > Pb > Zn > Cd > Fe > Mn > Ca > Sr > Ba$$

Other series and references to the original literature are presented by these authors. For monovalent cations with one ligand:

$$Ag > Tl > Li > Na > K > Pb > Cs$$

For tervalent cations:

$$Fe > Ga > Al > Sc > In > Y > Pr > Ce > La$$

The series for mono- and tervalent ions are rigorously applicable at present to only one oxygen containing ligand, and much more work for ions of these types must be done before these series are applied to ligands in general. The "natural order" sequence, on the other hand, appears, with few exceptions, to be very widely applicable.

Treatises by Martell and Calvin (1952), Bailar (1956), and Basolo and Pearson (1958) and the review article by Irving and Williams (1953) contain definitive discussions and references for chemical applications. Numerical values for stability constants have been collected (Bjerrum *et al.*, 1957). Two review articles by Williams (1953, 1959) and chapters in Bailar (1956) and Martell and Calvin (1952) are of great biological interest. The key function of iron complexes and their role in haeme proteins and oxygen transport (Wyman, 1948; Lamb *et al.*, 1958, Chapter 23) is well known. The importance of co-ordination phenomena in copper proteins (Dawson and Mallette, 1945; Lamb *et al.*, 1958, Chapter 21), zinc and metalloenzymes (Vallee, 1955; Lamb *et al.*, 1958, Chapter 22), metallic complexes with amino acids, peptides and proteins (Gurd and Wilcox 1956) has been discussed. The fascinating case of vanadium in the vanadocytes of the blood of *Acidians* has been outlined by Ralph (1954) (also Lamb *et al.*, 1958, Chapter 19). An examination of the structures of chlorophyll and haemin reveals that these substances are magnesium and iron complexes of the porphyrin family (Bailar, 1956, p. 74).

The geochemical importance of complexes such as those produced by the co-ordination of sulphide ion with the sulphides of As, Sb, Sn, Cu and Hg is obvious. Some other geochemical aspects of complex formation with reference to trace-element behaviour during magmatic crystallization have been discussed by Ringwood (1955b).

The treatment of co-ordination tendencies has been somewhat more detailed than that accorded to previous sections. In the writer's opinion this is justified since it is felt that co-ordination chemistry will make increasingly valuable contributions to geochemistry, biochemistry, and biogeochemistry (see Calvin (1959) for a discussion of enzyme evolution that appeared while this work was in press). One feature of the stability sequences is particularly noteworthy from the viewpoint of the geochemist. If these sequences are compared with the anion affinity sequences of Ahrens (1953) a striking parallelism becomes apparent.

Oxidation states and corresponding radii

Known stable and unstable oxidation states are summarized in Fig. 1. For each element the symbol z is used for oxidation state and r for the corresponding radius. Additional values are given in the table to the right of period 7 (see Fig. 1).

Oxidation states, in part, were obtained from scattered sources in the literature; but primarily from the excellent book by Moeller (1952). Ionic radii for co-ordination number 6 were chiefly taken from Ahrens (1952), although both Pauling (1940) and Goldschmidt (1954) were also consulted. After the table had been completed the writer found that a comprehensive new compilation (Sutton, 1958) recently had been published. In this work (Sutton, 1958) experimental values for interatomic distances based on a systematic search of the literature up to 31 December, 1955, are presented.

The single-bond covalent radii ($z = 0$) reported for various elements are taken from Pauling (1947). The single-bond radius, $R(1)$, is related to radius of bond order n by:

$$R(1) - R(n) = 0{\cdot}300 \log n$$

For metallic radii, co-ordination number 12:

$$R(1) - R(\text{c.n. } 12) = 0{\cdot}300 \log v/12$$

where v is the "valence". For non-transitional elements, the "valence" is the usual integral chemical valence, but for transitional elements Pauling uses non-integral values for v based on magnetic data. The original article should be consulted for details.

The following criteria were arbitrarily established for selecting the radii reported in Fig. 1.

(a) If the element has only one common oxidation state, the ionic radius for that state is given and the single-bond covalent radius from Pauling (1947).

(b) If the element has more than one oxidation state but it was felt that its behaviour in the biosphere was more dependent on covalent bond formation, the covalent radius and one oxidation state are reported (e.g. C and I).

(c) If the element is expected to function covalently in the biosphere and also has two or more common oxidation states with values for ionic radii reported (Ahrens, 1952) then the ionic radii are given (e.g. N, P, S). In these cases approximations to the covalent radii can be obtained by interpolation from values reported for neighbouring elements. Thus S would be expected to have a covalent radius between 1·2 (Si) and 0·99 (Cl). Actual value reported for S is 1·0.

(d) If the element (e.g. a transition element) has many oxidation states with reported values for ionic radii, then the highest and lowest oxidation states with corresponding radii are given. Rough values of r for intermediate states can be estimated by interpolation.

(e) A(-), appearing in the ionic potential (ϕ) space indicates that other common oxidation states are known.

(f) For the transition elements, the lanthanides, the actinides, and groups 3b–7b, known stable and unstable oxidation states are given in the table to the right of period 7 (see Fig. 1.)

GOLDSCHMIDT's empirical rules for predicting the geochemical fate of an element during crystallization from liquids provide an important example of the use of z and r data in geochemistry.

These rules can be summarized for two ions, 1 and 2, as follows:
(1) If $z_1 = z_2$ and $r_1 = r_2$, the ions will enter a given lattice with equal facility.
(2) If $z_1 = z_2$ but r_1 is slightly larger than r_2, ion 2 enters most readily.
(3) If r_1 is similar to r_2 but $z_1 > z_2$, ion 1 enters most readily.

Exceptions to these rules are encountered than can be rationalized in terms of other variables (see discussions of ϕ, e and I). Applications of radii in chemistry (MOELLER, 1952); in ion exchange (SAMUELSON, 1953); and in geochemistry (AHRENS, 1952) are available in the literature.

Ionic potential, ϕ, standard electrode potential, E, and ionization potential, I

The ionic potential, ϕ, is defined as z/r. Numerical values for this function calculated from z and r data in Fig. 1 are reported in the ϕ spaces.

Standard electrode potentials for the *oxidation* of metals according to the following equation:

$$M \rightarrow M^{+z} + z\, e^-$$

are listed in the E-spaces. For the halogens (7b) values corresponding to the reaction:

$$2X^- \rightarrow X_2 + 2e^-$$

are given. If the electrode process is not conventionally formulated by either of the above equations then the symbol c (for complex) is placed in the E-space. Large positive values of E are associated with elements that tend to release electrons readily in aqueous solutions. The electrochemical data presented in Fig. 1 were obtained from CONWAY (1952), MOELLER (1952), and LATIMER (1952).

First and second ionization potentials derived from MOELLER (1952), HERZBERG (1944) and AHRENS (1953) are given in the I-row. For the halogens the space normally used for the second ionization potential has been employed for electron affinity (HERZBERG, 1944).

Ionic potential (ϕ)

CARTLEDGE (1928a, 1930) has not only studied ionic potential and the periodic table, but also the relationship of this variable to acid-base behaviour of ions (CARTLEDGE, 1928b). This same author (CARTLEDGE, 1951) has correlated thermochemical data with the help of ionic potential data. In this last paper an ionic

potential defined as z divided by the univalent radius is employed. Mason (1958, p. 155) has presented a helpful discussion of the importance of ϕ in hydration and in sedimentary processes. Bailar (1956, pp. 120, 126, 423) and Martell and Calvin (1952, pp. 191–198) have outlined some applications in co-ordination chemistry. Hutchinson (1943, p. 336) has effectively employed the variable to rationalize the effect of solubility on the composition of terrestial plants. Kunin (1958, p. 29) has observed that the affinity of cations for ion exchange resins varies inversely with ϕ. Other items of geochemical interest are discussed by this same author.

In summary:

(1) Cations with similar ϕ's are frequently geochemically associated.
(2) Elements with $\phi \leqslant 4$–5 are electron-releasing, base formers that exist as soluble cations at ordinary pH.
(3) Elements with: $4–5 \leqslant \phi \leqslant 10–12$ are amphoteric and tend to form insoluble oxides or hydroxides.
(4) Elements with: $\phi \geqslant 10–12$ are electron-accepting, acid formers that tend to form soluble complex anions.
(5) In general, co-ordinating ability increases with increasing ϕ of the central cation.
(6) Cations of high ϕ are more polarizing and more highly hydrated than cations of low ϕ.
(7) The affinity of cations for exchange resins is inversely related to ϕ.

In Fig. 1 space did not permit inclusion of conventional Z, r and ϕ data for oxygen and the halogens. These are, respectively, O: 6, 0·10, 60; F: 7 (hypothetical), 0·08, 87; Cl: 7, 0·27, 26; Br: 7, 0·39, 18; I: 7, 0·50, 14 (see Ahrens, 1952). In Fig. 1 the reported, rather unconventional, negative values of ϕ for these elements correspond to high conventional positive values.

Ionization potential (I)

The importance of ionization potentials in inorganic chemistry (Moeller, 1952), co-ordination chemistry (Bailer, 1956; Martell and Calvin, 1952), biology (Williams, 1953), and geochemistry (Ahrens, 1953; Goldschimdt, 1954) has been stressed by several authors. In general:

(1) For cations of the same z, increasing I parallels increasing anion affinity and complex stability.
(2) Cations with similar ϕ's and similar I's are geochemically quite coherent.
(3) Elements with low I form soluble cations.
(4) Elements with very high I form soluble anions or are inert.

Space in Fig. 1 did not permit inclusion of I's for z's > 2. Ahrens (1953) has presented such data.

For $z = 3$: B-38, Al-28, Sc-25, V-26, Cr-32, Ga-31, Y-20, In-28, La-19, Tl-30.
For $z = 4$: C-64, Si-45, Ti-43, V-48, Ge-46, Zr-34, Sn-41, Ce-37, Hf-31, Pb-39.
For $z = 5$: N-97, P-65, V-65, V-65, As-63, Nb-52, Sb-56, Ta-45, Bi-56.

For $z = 6$: O-137, S-88, Cr-96, Se-82, Mo-70, Te-72, W-61.
For $z = 7$: F-184, Cl-114, Mn-122, Br-104, Tc-95, I-90, Re-79.

The original paper should be consulted for a critical analysis of these data.

Standard electrode potential (E)

A review of the application of E's in biology (George and Griffith, 1959), geochemistry (Mason, 1958), and chemistry (Latimer, 1952) can not be given in a single paragraph. The three references listed are, however, relevant and illustrative. A key point to recall in comparing e, ϕ, E and I is that E alone is derived from, and refers primarily to, processes occuring in aqueous solutions.

Acknowledgements—The writer is very grateful to The University of Texas Research Institute for a research leave that made possible the preparation of this paper and part II of the series. He would also like to express his appreciation to Professor E. Ingerson for helpful discussions of the geochemical aspects of this and other problems.

Studies in biogeochemistry—II

Discussion and references

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Abstract—A rule relating, within each periodic group, biological importance to ocean abundance is presented and discussed. Other biogeochemical relationships are analysed, and Frey-Wyssling's nutrient line is examined in the light of chemical developments. The possible existence of as yet unidentified nutritionally-essential trace elements is considered.

Earlier Work on Biogeochemical Periodicity

Thatcher (1934) was apparently the first investigator to examine the periodic behaviour of the biologically-essential elements. One of his conclusions was that the essential elements are limited to the first four periods (Mendeléeff-type periodic

table employed). He also proposed a useful division of these elements into eight groups. This classification was based on chemical properties (e.g. anion formers placed in one group).

Frey-Wyssling (1935) considered the elements (C, N, P, S, O, H, K, Mg, Ca, Fe, Mn, Cu, Zn and B) then known or suspected to play an important role in plant nutrition, and drew the *Nährstofflinie* on a Mendeléeff-type table (Fig. 2). This "nutrient line" is actually two lines with a common origin at carbon and four deep loops encircling Cu, Zn, Mn and Fe. One of the lines slopes downward to the left passing between B and Al, and between Mg and Ca to bisect K and terminate

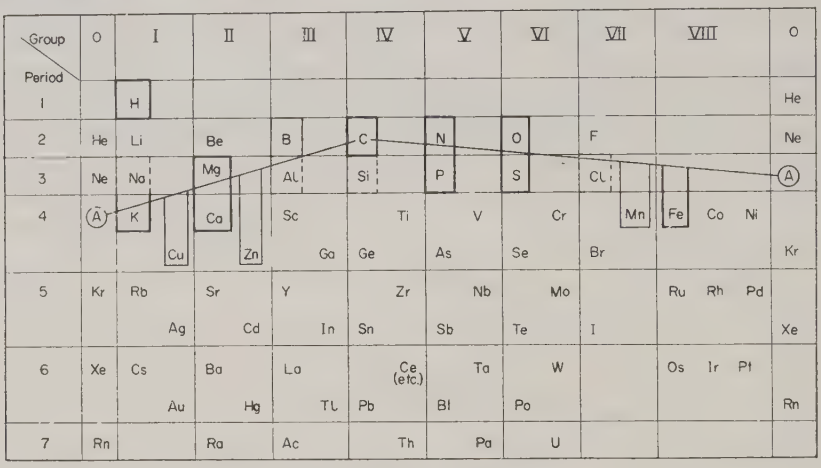

Fig. 2.

at A. A loop hanging from this line surrounds Cu. The second line slopes downward to the right passing between N and P, O and S, F and Cl. It then passes above the "looped" elements Mn and Fe to terminate again at A. Frey-Wyssling placed the inert gases on both the extreme left and extreme right of his table. On the right the entire group is displaced vertically upward by one element causing Ne (on the right) to be directly across from He (on the left). Frey-Wyssling's original article contains much information of general interest and references to the earlier literature. A good secondary source (Rankama and Sahama, 1950, Chapter 8) is also available.

Steinberg (1938) has written a provocative paper on correlations between biological essentiality and atomic structure. Using a periodic arrangement similar to Gardner's table (Moeller, 1952, p. 105) and based on subshell structure, he has come to the tentative conclusion that there should be three essential elements in each periodic group (e.g. Mg, Ca, Zn in Group 2). Stiles (1946, Chapter 4) has reviewed the literature on these earlier classifications.

The periodic variation of biospheric abundance has been considered by Vinogradov (1933), Webb and Fearon (1937) and Hutchinson (1943, pp. 331–336). Rankama and Sahama (1950, Chapter 8) and Mason (1958, Chapter 9) have also discussed the problem.

Chemical Nature of the Essential Elements

Nutritionists frequently simply list the essential elements in any convenient order (Maynard and Loosli, 1956, p. 108; Underwood, 1956, p. 2). The biogeochemical arrangement (Fig. 1, Part I) results in a natural segregation into three divisions.

I. The essential alkali and alkaline earth metals. Group 1a: Na(pA), K(EPA), and H(EPA). Group 2a: Mg(EPA), Ca(EPA), Sr(a), Ba(a).

II. The essential transitional metals.† Period 4: V(pa), Mn(EPA), Fe(EPA), Co(EPA), Zn(EPA). Period 5: Mo(EPa).

III. The essential non-metals. Group 3b: B(p). Group 4b: C(EPA), Si(?pa) Group 5b: N(EPA), P(EPA). Group 6b: O(EPA), S(EPA), Se(pa). Group 7b: F(a), Cl(pA), Br(a), I(A), and H(EPA).

The physicochemical characteristics of elements in these three divisions are presented in Table 1.

Table 1. Some physicochemical properties of essential elements in the three divisions

	Division I	Division II	Division III
e	$0{\cdot}91 \leqslant e \leqslant 1{\cdot}2$	$1{\cdot}4 \leqslant e \leqslant 1{\cdot}8$	$2{\cdot}0 \leqslant e \leqslant 4{\cdot}1$
ϕ	$0{\cdot}77 \leqslant \phi \leqslant 3{\cdot}0$	$1{\cdot}0 \leqslant \phi \leqslant 15$	$14 \leqslant \phi \leqslant 87$ (hypothet.)
	$0{\cdot}77 \leqslant \phi \leqslant 2{\cdot}0$ (without Mg)	$2{\cdot}3 \leqslant \phi \leqslant 15$ Cu^{I} omitted	
I_1	$4{\cdot}3 \leqslant I \leqslant 7{\cdot}6$ $4{\cdot}3 \leqslant I \leqslant 6{\cdot}1$ (without Mg)	$6{\cdot}7 \leqslant I \leqslant 9{\cdot}4$	$8{\cdot}3 \leqslant I \leqslant 17$
com	*of*, *n**	*of*, *n*, *n**, *ps*	o
Tentative complex stability sequence	K < Na		
	Ba < Sr < Ca < Mg < Mn < Fe < Co < Cu > Zn		Most frequently form ligands

Division I contains the low ϕ, electropositive elements that exist as cations in many water-soluble compounds. It is of considerable interest to note that Mg is the most electronegative element and forms the most stable complexes of elements in division I. From the viewpoint of both ϕ and I-data Mg might be expected to show properties in common with division II elements.

Division II contains elements of intermediate ϕ and e that form water insoluble compounds. These elements have, in general, partially filled d orbitals and are of established significance in catalysis.

Division III contains the electronegative, high ϕ elements that exist as anions in many water-soluble substances.

Abundance and Biological Importance

A useful rule. Biological importance can be measured by both biospheric

† Some authors (Moeller, 1952, pp. 102–103) classify the Group 1b and 2b elements as *representative* elements rather than as *transitional* elements. Classification of these elements is, as Moeller points out, largely a matter of choice.

abundance and nutritional essentiality. In each periodic group biological importance is related to both cosmic and crustal abundance as an examination of Fig. 1 (Part I) will reveal. Strongest correlation, however, is with oceanic abundance. Consequently, an important generalization can be made that the writer would like to propose as a useful working rule: *Within a periodic group, biological importance tends to parallel oceanic abundance.*

Division I. In periodic Group 1a, H, Na and K are biologically most important and are also found in greatest abundance in sea-water. Similar conclusions apply to Group 2a. Mg and Ca have the highest oceanic abundance. From the viewpoint of amounts structurally employed by some animals Ca is more important than Mg, but the key role of Mg in chlorophyll entitles it also to a position of utmost biological importance. It is of interest to note that Mg was probably selected for this function because it is not only highly abundant in the sea but also forms the most stable complexes of the oceanically-abundant elements. The high e, ϕ and I values for Mg would tend to imply biological function similar to the division II elements. The similarity of chlorophyll and haemin from the viewpoint of co-ordination chemistry has been noted in Part I of this series.

In both Groups 1a and 2a biological importance is almost as closely related to cosmic and crustal abundance as it is to oceanic abundance. This observation is quite reasonable since both the alkali and alkaline earth elements are strongly lithophile and hydrophile.

Division II. Groups 3a–8, 1b and 2b contain the essential "trace" transitional metals. Again, within a group, parallelism exists between biological importance and oceanic abundance.

The Group 6a elements might appear to be exceptional. At present Mo is classified as an essential element and Cr is not. It is quite probable that Cr may be essential† (see section on undiscovered essential trace elements). Vinogradov's (1953) data would indicate that Cr is more abundant than Mo in sea-water, but other investigators (see Harvey, 1955, p. 140) report the reverse. More research on this point is indicated (Richards, 1956).

A comparison of division II elements with those in division I is illuminating. Cosmically some of the essential "trace" transitional elements (e.g. Fe and Mn) are more abundant than "major" nutritional elements (e.g. Ca and K). The crustal abundance of Fe is similar to that of both Mg and Ca but the oceanic abundance of Fe and other "trace" metals is orders of magnitude less than that of the major nutritional metals Na, K, Mg and Ca. Thus from a biogeochemical viewpoint the division II essential elements are nutritionally "trace" elements because of pronounced chalcophile and siderophile character and low hydrophilicity. These geochemical characteristics are in turn related to physicochemical properties. Ionic potential (Hutchinson, 1943), electronegativity, and ionization potential (Table 1) are clearly intimately involved.

The "barren space". In considering the transitional elements it is of interest to point out the biologically-barren "peninsula" formed in the periodic table by elements 43–46 and 75–78. High-density (Os has the highest known density of any

† Please see footnote on p. 212.

element), strong siderophile tendencies, low abundance, extremely low hydrophilicity, negative E-values and general chemical nobility, high complex stability—these are the chief features of the "barren space" that is bounded on two sides by biologically-essential elements.

Division III. The elements in division III provide many tests of the oceanic abundance–biological importance correlation. In Group 3b, Al is more abundant than B in both the cosmos and the earth's crust; but, as far as is known, aluminium is not essential to life. Despite its cosmic and crustal disadvantage; B, a strongly hydrophile element, is needed by certain (and perhaps all) plants. The biogeochemistry of these elements has been eloquently discussed by HUTCHINSON (1943).

In Group 4b, oceanically–abundant carbon is biologically more important than crustally–abundant silicon. In fact Si has not been accepted as an essential element for animals by most authorities although it is used in shells of diatoms, skeletons of radiolaria, siliceous sponges, feathers of birds, and occurs in some woods in conjunction with cellulose. In plants some (UNDERWOOD, 1956, p. 2) state that it is definitely established as essential for higher plant life. ARNON (1958) does not list it as essential. MEHLICH and DRAKE (1955) class it as "beneficial".

The rule appears to hold quite well for the remaining periodic groups although present notions about the essentialness of bromine do not seem to be perfectly in line with predictions based on oceanic abundance.

THE NUTRIENT "LINE"

In a previous section it was pointed out that FREY-WYSSLING's (1935) nutrient "line" (Fig. 2) is actually two lines and four deep loops. The "line" was empirically drawn to pass near the elements then known to be essential for plants. It misses both Mo(EPa) and I(A), and very deep loops would be required to ensnare these elements with the *Nährstofflinie*.

The empirical need to employ loops can be attributed to the failure of the Mendeléeff table to provide adequately for transitional elements. The right branch of the *Nährstofflinie* can be generated by drawing a line of $I_1 = 13$, or $\phi = 25$, or $\epsilon = 2{\cdot}5$. The left branch is less well defined but corresponds roughly to a line of $I_1 = 7$. Thus the left branch is essentially aimed at the division I elements, the loops hold division II elements, and the right branch enters division III. In view of advances in nutrition (e.g. Mo), periodic classification, and knowledge of electronic structure that have taken place since FREY-WYSSLING's pioneering work; the *Nährstofflinie* in its original form must now be considered obsolete. A modified version of the right branch, however, appears to be of some importance. This line, the division II or essential non-metal line, can be generated in several ways.

If a line of $\phi = 13$ is inscribed on the biogeochemical periodic table (Fig. 1, Part I) it will originate at B, pass between Si and P, As and Se, Te and I, to terminate just above At. All the elements in Groups 3b–7b of well-established nutritional significance are found above this line. Elements like Si and As that have been suspected to play nutritionally–important roles as "trace" elements lie on the line.

An almost identical $I_1 = 10$ line can be drawn, and the $e = 2{\cdot}1$ line is very similar.

As Yet Undiscovered Essential Trace Elements

The temptation to interpolate and extrapolate is ever present; but conclusions reached by such processes applied to limited data must, of course, be viewed with caution. The following "predictions" must be regarded as of a suggestive but tentative nature.

Vanadium (Nason in Lamb *et al.*, 1958, Chapter 19) will become a well-established trace element. Nickel (Underwood, 1956, Chapter 6) will be found to play a role in a nutritionally significant co-ordination compound—probably associated with an enzyme. Chromium† will be similarly implicated. The neglected element, titanium, may soon be recognized as essential to the life of plants and animals.

Elements lying near the essential non-metal line (see preceding section) such as Al, Si and especially As may be assigned hitherto unsuspected roles in living organisms. Rb (Underwood in Lamb *et al.*, 1958 p. 37) and Li merit further investigation. Steinberg's (1938) conclusions concerning the essential nature of Ga in plants would also suggest that additional work with this element should be done.

Rare earths are reported (Monier-Williams, 1949, p. 494) to be: essential for the normal development of peas, stimulatory to the growth of certain plants, capable of partially replacing calcium; and to occur in bones. These elements are found in hickory trees (Robinson *et al.*, 1958) and are enriched in plants (Hutchinson, 1943, p. 341). Although Vallee (1955, p. 327) failed to recognize the occurrence of these elements in living tissues; he noted that other investigators had observed that Nd, La and Sm activate the succinoxidase system. These observations, the lithophile character of rare-earths, and their abundance in sea-water and the earth's crust at levels approaching the established division II elements, would indicate that an important biological function for the lanthanide elements may eventually be established.

Concluding Remarks

On the biogeochemical periodic table the elements form many intriguing patterns. The areas containing the essential metals and the other area in which are found the essential non-metals bounded by the $\phi = 13$ line have been described. In marked contrast to these fertile regions; the "barren space" stretches its siderophile length from the synthetic transuranic elements toward the essential trace metals: manganese, iron and cobalt.

In Part I of this series it was pointed out that availability and chemistry are important twin criteria in understanding the biochemistry of evolution. Comparing biological importance with the relative oceanic abundance of elements in a periodic group corresponds approximately to examining the effect of availability under conditions of "constant" chemistry. Such a comparison, as we have seen, results

† Note added in proof. This prediction apparently has been realized. Schwartz and Mertz (Nov. 1959) conclude: "The fact that Cr(III) is necessary for maintenance of a normal glucose tolerance appears to indicate that it may be a bioelement essential for mammalian organisms".

in the useful rule discussed in the section on abundance and biological importance. This relationship seems to be of broad significance, and it will be demonstrated in a subsequent paper that correlation exists between experimentally-determined, quantitative, nutritional requirements and oceanic abundance. Preliminary analysis also indicates that, *within a periodic group, toxicity and oceanic abundance are inversely related.* Thus even for the biosphere, we can conclude with SUESS and UREY (1956) "that matter surrounding us bore signs of representing the ash of a cosmic nuclear fire in which it was created". We can further assert that nutrient requirements, toxicity and the composition of living things are related to the composition of a solution formed by leaching the ashes of this primordial conflagration.

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Production of tritium in nuclear spallations

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Abstract—Production cross-sections for tritium have been measured in cyclotron targets and have been quoted as 53, 62 and 130 millibarns. These are compared with values deduced from cosmic-ray bombardment of iron meteorites, where a direct tritium measurement leads to 280 mb, while He^3:He^4 ratio measurements lead to at least 215 mb, possible as high as 410 mb. Hence application of cyclotron cross-sections may lead to too high values for the cosmic-ray ages of meteorites.

The production of tritium in nuclear spallations is of importance for many astrophysical studies. Some time ago, therefore, the writer calculated the rate of tritium production by cosmic rays in iron meteorites, and derived a value of 8×10^{-3} tritons per g per sec at the cosmic ray transition maximum (2–15 cm from the "preatmospheric" meteorite skin) (Singer, 1953). This calculation was based on an earlier one (Singer, 1952) for the production rate of He^3 and He^4 and made use of data on cosmic-ray "stars" and results of nuclear evaporation theory.

However, experimental checks of iron samples exposed in cyclotrons have given consistently low values: a tritium production cross-section $\sigma = 62 \pm 7$ mb for 2 BeV protons (Fireman, 1955); $\sigma = 53 \pm 8$ mb for 2·05 BeV protons (Currie *et al.*, 1956) which would correspond to a "cosmic-ray" production rate of only $8{\cdot}8 \times 10^{-4}$ tritons per g per sec under the same conditions as above.

The discrepancy has been puzzling us for some time. We saw no reason for revising our calculation, and there seemed to be nothing obviously wrong about the measurements. We have given some arguments* why more tritium would be produced if the energy of the protons were raised. Additional experimental evidence has been produced. For example, Fireman and Zähringer (1957) quote $\sigma = 130$ mb at 6·2 BeV, which, however, is still low.

More direct evidence can be obtained from the meteorites themselves under actual cosmic ray bombardment. For example, Begemann *et al.* (1957) measure a tritium activity corresponding to a production rate of $4{\cdot}7 \times 10^{-3}$ calculated for the transition *maximum*.

Another approach is through the recent work of Schaeffer and Zähringer (1959). They quote σ (for He^4) = 1300 mb,† σ (for He^3) = 240 mb at 3·0 BeV. If we now combine this result with the maximum He^3:He^4 ratio measured so far in iron meteorites (Dalton *et al.* 1953) of 0·35 (where of course the He^3 includes all of the decayed tritium), we derive immediately that $\sigma(H^3)$ is 215 mb. With the use of a "primary" He^3:He^4 ratio of 0·50 suggested by Hoffman and Nier (1959),

* Nuclear, as well as astronomical, arguments can be given (Singer, 1958). The astronomical consequence of a low measured rate is an unreasonably high lifetime of the meteorites in the solar system.

† This corresponds to a He^4 production rate (at the transition maximum) of $2{\cdot}2 \times 10^{-2}$ atoms per g per sec, or $2{\cdot}6 \times 10^{-14}$ cm³ (s.t.p.) of He^4 per g per year. Thus the He^4 result is in excellent accord with our calculated value of $(3{\cdot}5 \pm 1{\cdot}0) \times 10^{-14}$ cm³ per g per year (Singer, 1952).

$\sigma(H^3)$ becomes 410 mb.* The corresponding production rate would be 7×10^{-3} tritons per g per sec, very close to our calculated value (Singer, 1953) of 8×10^{-3}.

We conclude that the tritium production rates measured in accelerators may be too low by a factor ranging from 2 up to perhaps 4, at least when translated to cosmic-ray effects on meteorites. It seems to us still important to measure the depth variation of the tritium activity in a recently fallen meteorite, together with the He^3 and He^4 content, in order to arrive at a self-consistent calibration for these important production rates.

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* A ratio $\sigma(H^3)$: $\sigma(He^3)$ of 2:1 is also suggested by evaporation theory (Le Couteur, 1950).

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Flame photometric determination of strontium in silicates. Strontium content of the granite G–1 and the diabase W–1

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Abstract—A method for the determination of strontium in silicate materials by flame photometry is described, based on the standard addition technique. It takes background emission measurements into account and, where necessary, high concentrations of calcium salts are added to compensate for the depressing effect of aluminium.

With this method, a strontium content of 258 p.p.m. in granite G–1 and of 151 p.p.m. in dibase W–1 was found. Precision and accuracy of the method are discussed.

Flame photometry allows precise and accurate determination of strontium in cements (Diamond, 1955) and in sea-water (Chow and Thompson, 1955). In this paper, an attempt is made to extend the use of flame photometry to the determination of strontium in silicates. The procedure in question is somewhat different from the method proposed independently by Debras and Voinovitch (1959) and is based on the standard addition technique as described by Diamond (1955) and Chow and Thompson (1955).

The method allows a rapid determination of the elements in a solution which can also be used for the determination of other elements by flame photometry or other methods.

The method was checked against granite G–1 and diabase W–1 standards; the obtained results are characterized by a good repeatability and compare favourably to the average of the best spectrographic determinations and stable isotope dilution data.

The chief drawback of flame photometric determination of strontium is the interference of aluminium which, as is known, has a strong depressive effect on Sr-emission, due to the formation of a molecular strontium aluminate. This effect would actually not be disturbing, since with the standard addition technique, the sample and standard solutions have exactly the same composition as far as the interfering elements are concerned, but in practice the instrumental readings drop too low, so that errors become important.

This difficulty can easily be overcome by taking advantage of the compensating effect of calcium (Burriel-Martì, 1957), as described below.

The Method

Reagents and apparatus. Perchloric acid 70 per cent strength. Hydrofluoric acid 40 per cent strength. Standard Sr-solution: prepare a Sr-solution containing 25 p.p.m. SrO from pure $SrCO_3$ dissolved in HCl. Calcium solution: prepare a Ca-solution containing 10,000 p.p.m. Ca from the purest $CaCO_3$ dissolved in HCl.*

* If no spectrochemically pure $CaCO_3$ is available, the Sr content of $CaCO_3$ is to be determined and a correction must be made in the following calculations. In our experiments, we used a $CaCO_3$ containing 100 p.p.m. SrO.

Beckmann DU flame photometer with photomultiplier attachment and power supply no. 23701. The flame photometer is operated with oxyhydrogen flame, slit width = 0·04 mm, sensitivity switch on the photomultiplier control panel at position 7, selector switch 0·1, sensitivity control on the left panel of the instrument from 0 to 3 turns from its counterclockwise limit.

Operating under the described conditions, the Sr-emission at 461 mμ was found to be linear in the range of 0–10 p.p.m. Sr.

Procedure. A weight of 1 g of the powdered sample is decomposed in a 50 cm^3 platinum crucible with a mixture of 5 ml of perchloric acid and 20 ml of hydrofluoric acid. Warm on a steam bath for 2 hr, then carefully evaporate to dryness on a sand bath. Add 3 ml of perchloric acid, repeat evaporation until copious white fumes escape, then dissolve the residue with hot water. Transfer to a 50 ml graduated flask, add, if necessary, 10 ml of Ca-solution, and make up the volume with distilled water.* Take an aliquot of 25 ml, transfer to a 50 ml flask, add 10 ml of the standard Sr-solution and make up the volume with distilled water (solution 2). This solution will contain x + 5 p.p.m. SrO. The remaining 25 ml of the solution, contained in the first 50 ml flask, are brought to the required volume with distilled water (solution 1). This solution will contain x p.p.m. SrO.

Bring solution (2) into the flame and record the value of the emission $(E_2)_{461}$ at 461 mμ as read on the $\%T$ dial; subtract the average of the readings taken at 454 and 463 mμ and record the value

$$E_2 = (E_2)_{461} - \frac{(E_2)_{463} + (E_2)_{454}}{2}$$

Repeat the procedure bringing solution (1) into the flame and record the value

$$E_1 = (E_1)_{461} - \frac{(E_1)_{463} + (E_1)_{454}}{2},$$

Calculate the strontium content x of the unknown solution by the formula

$$x \text{ p.p.m.} = \frac{5\,E_1}{E_2 - E_1}$$

In order to minimize the errors, the amount of SrO added to the solution need not be fundamentally different from the amount to be determined. This can easily be done if one knows the order of magnitude of the expected Sr content of the sample or otherwise by means of a preliminary measurement. Should the Sr content of the sample solution be fundamentally different from 5 p.p.m. repeat the procedure using adequate weighing of the sample or appropriate dilutions.

Experimental Results

Strontium content has been determined on granite G–1, diabase W–1 and on a specimen of melilite–leucitite from Capo di Bove, Alban Hills, Rome. For the diabase and leucitite, no addition of calcium proved to be necessary since in the first case the rock contains enough calcium to ensure a sufficient sensivity to Sr-emission, and in the second case both calcium (10·5% CaO) and strontium contents of the rock are high.

For purpose of comparison, strontium content in granite G–1 with low Ca percentage (1·4% CaO) was determined in two different ways: with and without addition of Ca-solution.

Table 1 shows the results of the measurements. Each rock was analysed five times taking five independent 1 g weighings. Each value represents the average of

* In the case of silicates having a high potassium content, it is advisable to operate with higher dilution in order to prevent a separation of crystalline $KClO_4$.

five instrumental readings. From the data of the Table 1 the usefulness of Ca-addition in the case of granite G–1 becomes evident through the fact that the standard deviation drops from 15·6 (6 per cent) to 5 (2 per cent), because the instrumental readings are more precise. Nevertheless, the determination of strontium in rock containing as little as 1·4% CaO is still possible, even without the addition of calcium, due to the very high sensitivity of the instrument.

Table 1.

		Without addition of CaO		With addition of CaO	
		p.p.m. Sr	σ = standard deviation c = relative error	p.p.m. Sr	σ = standard deviation c = relative error
G –1	1	247		259	
	2	265	$\sigma = 15{\cdot}6$	257	$\sigma = 5{\cdot}08$
	3	244	$c = 6{\cdot}05\%$	265	$c = 1{\cdot}97\%$
	4	282		251	
	5	252		260	
	Average	258		258	
W –1	1	148			
	2	154	$\sigma = 4{\cdot}9$		
	3	158	$c = 3{\cdot}25\%$		
	4	149			
	5	144			
	Average	151			
Leucitite	1	1475			
	2	1385	$\sigma = 36{\cdot}67$		
	3	1425	$c = 2{\cdot}58\%$		
	4	1435			
	5	1390			
	Average	1422			

Table 1 shows that a very satisfactory precision is achievable in the range from 100 to 1500 p.p.m. Sr: the percentage standard deviation varies from 2 to 3·25 per cent.

The flame photometric determination of Sr indicates a value of 258 p.p.m. in granite G–1 which is consistent with the value of 237 p.p.m. representing the average of all spectrographic measurings (Table 2) except the abnormal value of 900 p.p.m. If one disregards also the value of 120 p.p.m., the average of the spectrographic measurings rises to 260 p.p.m. in close accordance with the flame photometric determination. Our value also shows very close accordance with the more recent value obtained by Turekian *et al.* (1957) by means of the stable isotope dilution technique.

The strontium content of diabase W–1, as determined by flame photometry, is 151 p.p.m. This value, although still in agreement with the average of all spectrographic (167 p.p.m.) and stable isotope dilution determinations (177 p.p.m.), shows a slightly more pronounced difference.

The strontium content of the leucitite rock averages 1422 p.p.m. with a standard deviation of 2·58 per cent, showing a good precision even in the range of 1500 p.p.m.

Table 2.

Analyst	Method	W–1 diabase p.p.m. Sr	G–1 granite p.p.m. Sr
(1) Herzog and Pinson (1955)	Stable isotope dilution	182 172	230 233 236
(2) Turekian (1957)	Stable isotope dilution	178	262
	Average	177	240
(3) Ahrens *et al.* (1954)	Optical spectrograph	250	250
(4) Mitchell*	Optical spectrograph	420	900
(5) Nockolds*	Optical spectrograph	180	280
(6) Murata*	Optical spectrograph	120	120
(7) Harvey*	Optical spectrograph	180	220
(8) Turekian (1955)	Optical spectrograph	110	265
(9) Turekian *et al.* (1957)	Optical spectrograph	172	287
	Average excluding (4)	167	237
	Average excluding (4), (6)		258
(10) Fornaseri and Grandi (this paper)	Flame photometry	151	258

* Quoted by Ahrens (1954)

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Relationships between geology and composition of some pegmatitic monazites*

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Abstract—Fourteen monazites from several well-studied pegmatites and pegmatite districts in the western states have been analysed by X-ray fluorescence spectrometry for the cerium subgroup of rare-earth elements, as well as yttrium and thorium. The results have been correlated with the paragenesis, mineralogy and geology of the occurrences. They show several distinct, and in some cases unique, rare-earth element distributions which are characteristic not only of individual pegmatites but also of entire pegmatite districts.

Introduction

Within the last fifteen years there have appeared many new analyses of monazites in which individual rare-earth elements have been determined. Among the more significant results are those reported by Borovsky and Gerasimovsky (1945), Wylie (1950), Murata *et al.* (1953, 1957), Vainshtein *et al.* (1955, 1956a, b), and Semenov and Barinskii (1958). With a few exceptions the monazites analysed were selected from a wide geological variety of deposits and from many widely-separated localities. Few data are available to test the compositional variation of monazites from a single deposit or from a group of related deposits. Murata *et al.* (1957) have analysed outer and inner parts in each of two crystals, one from Grama, São Paulo, Brazil, and the other from Hitterö, Norway. They have also analysed five monazites from the Shelby district, North Carolina; two are from quartz monazite pegmatite and three from the parent quartz monazite. Murata *et al.* (1958) have reported on the compositional variation in monazites from two Brazilian pegmatites.

The objectives of this study were to determine the compositions of a group of monazites whose occurrences were accurately known, in order to obtain data on the following problems:

1. Whether different specimens of paragenetically identical monazite from a single deposit are compositionally identical or similar.
2. Whether specimens of paragenetically identical monazite from different pegmatites in a single district show any compositional variation.
3. General compositional variations within pegmatite districts.

The fourteen monazites analysed in this study are all pegmatitic in origin and all but one were collected personally by Heinrich from deposits in districts in the western United States (Table 3).

* Contribution from the Department of Mineralogy, The University of Michigan, Ann Arbor, Michigan, No. 232.

X-Ray Fluorescence Analysis for Rare-earth Elements in Monazites

X-ray fluorescence spectrometry was used for the analysis of rare-earth elements in the monazites. The elements determined were lanthanum, cerium, praseodymium, neodymium, samarium, gadolinium, yttrium and thorium, which is commonly present in significant amounts. Based on previous work of a similar nature, the accuracy of the method is within ± 10 per cent of the amount present for the less abundant elements and ± 5 per cent of the amount present for the more abundant elements (La, Ce, Nd, Th).

Equipment

The standard Philips Electronics X-ray fluorescence equipment used in this work consisted of the 60 kV, 50 mA power supply with voltage and amperage stabilizers. A FA-60 tungsten target tube was the X-ray source, and the analysing crystal was lithium fluoride having a $2d$ spacing of 4·028 Å. No collimation was used between the sample and the analysing crystal, but the standard 800-plate collimator was placed between the crystal and the Geiger tube detector. The diffractometer was fitted with a helium path attachment. Sample holders of plexiglass were $1\frac{1}{4}$ in. wide, $1\frac{3}{4}$ in. long by $\frac{1}{4}$ in. thick, with a cavity $\frac{3}{4}$ in. wide and $1\frac{1}{4}$ in. long by $\frac{3}{16}$ in. deep. The Philips Electronics circuit panel was equipped with a recorder for qualitative scanning and counting circuitry for quantitative determinations.

Preparation of samples and standards

A weighed amount of the 400-mesh monazite, usually 0·250 g, was digested with 10 ml concentrated sulphuric acid and finally taken to dryness. To this was added 9·750 g of acid-washed SiO_2 of 400-mesh size, and the mixture was then ground in a suitable ceramic mortar until a completely uniform sample was obtained. Uniformity was determined by periodically examining a sample by means of X-ray fluorescence until reproducible intensities were obtained for one or more of the elements under examination. Standards consisting of known amounts of the several elements were made up in a similar manner in SiO_2. The concentration of the standards varied from 0·5 per cent by weight for lanthanum and cerium to 0·1 per cent by weight for yttrium.

For the sample size of 0·250 g and the amount of SiO_2 (9·750 g), a dilution factor of 1:40 was obtained. This reduced the amount of any element to a reasonably small concentration in the sample and thus minimized any absorption edge or enhancement effects.

Procedure

Samples and standards were firmly packed into the plastic holders to form a smooth, dense surface which could be easily reproduced. The holder was then placed into the beam of X-rays and the helium stream was turned on. The diffractometer was manually set to the predetermined angle for the desired element, and the signal was measured on the count register. Background measurements were made in a similar manner at a 2θ setting in a clear region as close as possible to the 2θ setting for the sample. Suitable counting times were used so as to obtain

statistically meaningful data. Table 1 contains the data as determined on monazite specimen no. 5201. The power factors used were 45 kV and 25 mA for all elements except thorium. The standard used for thorium was best handled at 45 kV and 15 mA.

Cerium was the only element which would not produce a strong line in a clear region. The best line for this element was superimposed upon the tungsten L_{B_1} second-order line. The contribution for this tungsten order was determined and

Table 1. Analytical data for specimen no. 5201

Element	°2θ peak	°2θ background	Peak (counts/sec)	Background (counts/sec)	Net (counts/sec)	(Standard) per unit of element in SiO_2	Dilution conversion factor	% element as oxide in monazite
La	82·93	81·00	64	32	32	68/0·5% La	40	11·0% La_2O_3
Ce	79·08	81·00	136*	32	104	82/0·5% Ce	40	29·7% Ce_2O_3
Pr	68·32	67·40	56	37	19	48/0·2% Pr	40	3·7% Pr_2O_3
Nd	65·22	62·00	140	43	97	63/0·2% Nd	40	14·4% Nd_2O_3
Sm	59·64	62·00	83	43	40	106/0·2% Sm	40	3·5% Sm_2O_3
Gd	54·74	50·00	82	63	19	104/0·1% Gd	40	0·8% Gd_2O_3
Y	23·97	23·00	187	73	114	197/0·1% Y	40	2·9% Y_2O_3
Th	27·64	26·90	136	43	93	116/0·2% Th	40	7·3% ThO_2
							Total	73·3%

* Net counts after correction for signal from second-order tungsten L_{B_1}.

the total signal was corrected by this amount. The cerium standard was corrected in a like manner, and suitable data for cerium were thus obtained. The use of pulse-height discrimination in conjunction with a scintillation counter would simplify the determination for cerium.

Geology of the Specimens

Petaca District, New Mexico

The geology and mineralogy of the Petaca pegmatites have been described by Jahns (1946). The pegmatites possess well-developed zones and albite-rich replacement units. Characteristic and widely-distributed accessory minerals are garnet, green and purple fluorite, columbite, monazite, samarskite, cyrtolite, ilmenite, beryl and rose muscovite (Henrich and Levinson, 1953). Monazite, which has been found in fifty-seven deposits or 83 per cent of all deposits examined, is closely associated with columbite, samarskite and purple fluorite in strongly albitized parts of pegmatites. The monazite varies in size from microscopic grains to masses about 6 in. across, weighing as much as 9 lb. The mineral commonly is a medium reddish brown in colour. The formation of the monazite is part of the mineralization accompanying the extensive albitization, and the monazite is believed by the writer (Heinrich) to be of hydrothermal origin.

Monazites from the following deposits were analysed:

1. North Star pegmatite. Tablets occur up to 1 in. long and ½ in. thick Analyses nos. 5185, 5186, 5187.

2. Coats pegmatite. Blocky crystals from 2 to 6 in. across. Analyses nos. 5188, 5197.

3. Fridlund pegmatite. Tablets as much as 1 in. in length. Analysis no. 5189.

Elk Mountain District, New Mexico

The Elk Mountain district, in San Miguel County, also has been studied by Jahns (1946). Monazite from a pegmatite near the head of Manzanares Creek between Cow Creek and Bull Creek, 14 miles north-east of Pecos, has been analysed (no. 5190). The dikes in this part of the district are zoned and locally albitized, containing accessory spessartite, fluorite, columbite and monazite. Gadolinite also is reported. These accessories are associated with secondary albite, and the monazite is regarded as similar in origin to that of the Petaca district.

Brown Derby Pegmatites, Colorado

The Brown Derby pegmatites in the Quartz Creek district of Gunnison County have been intensively studied (Hanley *et al.*, 1950; Staatz and Trites, 1955). Monazite has been found in twenty-six pegmatites in the district, or about 1·4 per cent of those studied. It occurs in unzoned, zoned and complex pegmatites, chiefly in wall zones and intermediate zones. Common associates are quartz, oligoclase–albite, microcline, muscovite and black tourmaline. Three monazites from this district were analysed (nos. 5195, 5196, 5202). Their occurrence and geology are as follows:

No. 5195. Monazite in excellent euhedral crystals as much as 2 in. long, 1 in. across and 0·4 in. thick, in the eastern arm of Brown Derby no. 2. This occurrence is referred to by Staatz and Trites (1955, p. 76) as being in the Brown Derby no. 1 dike (their no. 452) but actually is in a split from the southern end of Brown Derby no. 2 (their no. 453). The unit, formerly exposed only in pit no. 11, forms a lens about 1 ft thick and not more than 20 ft long. It contains chiefly albite with less abundant quartz, and accessory zinnwaldite, spessartite, gahnite, blue tourmaline, monazite and columbite. The unit, which is estimated to contain 2·2 per cent monazite and 1·4 per cent columbite (Staatz and Trites, 1955, p. 76), is separated from the hanging wall contact by a 4 to 6 in. border zone chiefly of albite and quartz. Structurally the unit represents a mineralogically unusual phase of the wall zone, localized beneath a structural roll in the hanging wall contact.

No. 5196. Monazite in anhedral pods as much as 4 in. across in the northern part of the Brown Derby no. 1 pegmatite. The mineral occurs in the wall zone consisting mainly of albite, quartz, microcline and muscovite, associated with clusters of muscovite books and corroded by aggregates of schorl.

No. 5202. Monazite in small $\frac{1}{2}$ in. tablets from small pegmatite, Brown Derby no. 7 (Staatz and Trites, 1955, no. 458) north of Brown Derby no. 2, containing albite, quartz, microcline, muscovite, and a trace of beryl.

In all three of these occurrences the monazite is in wall-zone rock and is believed to be magmatic in origin.

Trout Creek Pass Area, Colorado

The zoned pegmatites in the Trout Creek Pass area, in Chaffee County, contain accessory euxenite, allanite monazite, fluorite, haematite, garnet, apatite and anatase (pseudomorphous after ilmenite). The monazite, which is closely associated with fluorite and euxenite, forms tabular masses as large as 4·5 × 2·5 × 2 in. (Heinrich, 1948). These minerals occur in small masses of albite-rich pegmatite

Table 2. Analyses of monazite (wt. %)

	5185 North Star, Petaca, N.M.	5186* North Star, Petaca, N.M.	5187 North Star, Petaca, N.M.	5188* Coats, Petaca, N.M.	5197 Coats, Petaca, N.M.	5189 Fridlund Petaca, N.M.	5190 Pecos, N.M.	5195† Brown Derby no. 2, Colo.	5196* Brown Derby no. 1, Colo.	5202 Brown Derby no. 7, Colo.	5191 Yard, Colo.	5193 Luella, Colo.	5200 Baumer, Colo.	5201 Baumer, Colo.
La_2O_3	9·9	11·0	9·7	11·7	10·4	11·7	8·7	6·9	5·8	6·2	9·0	9·0	8·7	11·0
Ce_2O_3	26·6	27·6	26·5	27·7	27·4	29·1	27·1	28·0	27·0	25·4	26·2	28·6	28·3	29·7
Pr_2O_3	2·9	3·3	2·9	3·3	3·1	3·3	3·1	4·1	3·9	3·5	2·9	3·3	3·3	3·7
Nd_2O_3	12·6	12·5	11·6	12·6	13·1	13·2	13·0	18·2	16·8	17·6	12·7	13·3	12·8	14·4
Sm_2O_3	5·2	3·8	4·5	3·9	3·8	3·9	3·5	7·9	11·7	6·5	3·5	3·4	3·4	3·5
Gd_2O_3	1·8	1·2	1·7	1·3	1·5	1·7	0·6	2·9	4·1	2·0	1·0	1·0	0·7	0·8
Y_2O_3	0·8	0·8	0·6	1·0	0·5	1·4	0·4	2·2	2·3	2·3	2·0	2·0	2·9	2·9
ThO_2	10·7	11·8	11·2	10·4	9·5	7·7	9·9	4·0	4·1	3·8	10·1	9·2	7·1	7·3
Total	70·5	72·0	68·7	71·9	69·3	72·0	66·3	74·2	75·7	67·3	67·4	69·8	67·2	73·3
						Minor and Trace Elements‡								
CaO	0·5	0·5	0·5	0·5	0·5	0·5	n.d.	n.d.	n.d.	0·5	0·5	0·5	0·5	0·5
FeO	0·5	0·5	1·0	1·0	0·5	0·5	0·5	0·5	0·5	0·5	3·0	3·0	1·0–2·0	0·5
PbO	0·2	0·2	0·2	0·2	0·2	0·2	0·2	0·1	0·2	0·2	0·2	0·2	0·2	0·2
U_3O_8	n.d.§	n.d.	n.d.	0·1	0·1	n.d.	0·1	0·1	n.d.	n.d.	n.d.	n.d.	0·1	0·1
Σ(La + Ce + Pr)	66·3	69·8	68·4	69·9	68·9	68·5	69·3	55·6	51·4	55·4	66·1	67·1	66·3	66·5
Ce/(Nd + Y)	1·98	2·06	2·17	2·02	2·02	1·92	2·03	1·33	1·36	1·24	1·70	1·79	1·69	1·62

* Average of two determinations.
† Also contains estimated 1·0% TiO_2.
‡ Estimated wt. % with maximum limit given.
§ n.d. = not detected.

formed by replacement of marginal parts of quartz–microcline cores. Two monazites from dikes in this area have been analysed: no. 5191 from the Yard pegmatite and no. 5193 from the Luella pegmatite (Heinrich, 1948).

Guffey Area, Colorado

One pegmatite in the Guffey area in Park County, the Baumer pegmatite (Heinrich and Bever, 1957), contains accessory euxenite, monazite, allanite, and radioactive ilmenite. The monazite (nos. 5200 and 5201) forms euhedral to subhedral crystals, as large as $1\frac{1}{8} \times 1 \times \frac{1}{8}$ in., closely associated with euxenite or intergrown with it, in wall zone rock close to contacts with a quartz–microcline core. The wall zone contains mainly microcline, oligoclase, quartz and biotite. The monazite and euxenite are primary constituents of this unit.

Results of Analyses and Discussion

The analytical results are presented in Table 2. Descriptions of the analysed monazites are given in Table 3. Noteworthy relations in these analyses are:

(1) In all monazites, Nd > La. This is the first set of analyses to show consistently Nd > La since the initial work of Goldschmidt and Thomassen (1924) on Norwegian monazites (although about 10 per cent of the analyses in the literature have this relationship). Furthermore, the Nd/La ratio appears to be a district or "regional" characteristic of rare-earth distribution.

(2) In the three Brown Derby examples, Sm > La. No other analyses of monazites in the literature show this distribution.

(3) In all cases, Sm > Pr. This distribution has been previously noted only rarely in monazites.

(4) A very limited range of Ce and Pr.

(5) A wide range of Y, Gd and Th.

It is also noteworthy that the quantity sigma (Σ), which is the sum of the atomic percentages of La, Ce and Pr proposed by Murata *et al.* (1953) as an index for the composition of cerium-earth minerals, is in the range 51–55 for the three Brown Derby monazites, the previously reported low being 58. The low sigma value means these monazites are considerably enriched in the heavier lanthanides in comparison to most other monazites. The possibility that available lanthanum may have been captured in potassium minerals was considered, but none (our limit of sensitivity is estimated to be 25 p.p.m.) was found by emission spectroscopy in microcline, cleavelandite or muscovite, as well as in euxenite from these pegmatites. The relatively-low contents of La and Pr with the corresponding abundance of Nd and Sm in these samples is perhaps analogous to some monazites noted by Vainshtein *et al.* (1956b), from Fennoscandavia and other areas. They noted a "pegmatitic effect", in which there was a significant enrichment of Sm and the heavier rare earths and a decrease in La and Ce in certain pegmatitic monazites in comparison to monazites from the parent granites. Although no monazite has been reported from the parent granite of the Brown Derby pegmatites, an analysis of such a monazite seems desirable.

Inspection of analyses 5185, 5186, 5187 (Table 2) from the North Star pegmatite shows that specimens of paragenetically identical monazites from a single pegmatite

are remarkably uniform in their rare-earth composition. These analyses show also that there is about the same order of variation between the two composite samples (5185, 5186) as there is between the composites and the single-crystal sample (5187). This is in accord with results by Murata *et al.* (1957), who showed that analysis of duplicate samples of monazites (their nos. 6 and 19) from quartz monzonite in the Acre Rock quarry, Shelby district, North Carolina, gave very close results for the

Table 3. Description of analysed specimens

No.	Locality	Description	Origin
5185	North Star pegmatite, Petaca dist., N.M.	Composite sample from many crystals and grains; light brown.	Replacement
5186	North Star pegmatite, Petaca dist., N.M.	Composite sample from many crystals and grains; medium brown.	Replacement
5187	North Star pegmatite, Petaca dist., N.M.	Part of a single crystal dark brown.	Replacement
5188	Coats pegmatite, Petaca dist., N.M.	Composite sample from several crystal fragments.	Replacement
5197	Coats pegmatite, Petaca dist., N.M.	Fragment from a single large crystal.	Replacement
5189	Fridlund pegmatite, Petaca dist., N.M.	Fragment from a single crystal.	Replacement
5190	Manzanares Creek, Pecos, N.M.	Fragment from a single crystal.	Probably replacement
5195	Brown Derby no. 2 pegmatite, eastern arm, Gunnison Co., Colo.	A single euhedral crystal.	Magmatic
5196	Brown Derby no. 1 pegmatite, Gunnison Co., Colo.	Part of a large single corroded crystal.	Magmatic
5202	Brown Derby no. 7 pegmatite, Gunnison Co., Colo.	A single crystal.	Magmatic
5191	Yard pegmatite, Trout Creek Pass, Colo.	Composite from several crystal fragments.	Replacement
5193	Luella pegmatite, Trout Creek Pass, Colo.	Composite from several crystal fragments; dark brown.	Replacement
5200	Baumer pegmatite, Guffey area, Colo.	Part of single subhedral crystal.	Magmatic
5201	Baumer pegmatite, Guffey area, Colo.	Part of single subhedral crystal; closely associated with euxenite.	Magmatic

rare earths. Their results show a much greater ThO_2 variation (10·9 and 7·7 per cent) than do ours (10·7, 11·8 and 11·2 per cent).

Similarly a comparison of the two analyses (5188, 5197) of Coats monazite and of the two analyses of Baumer monazite (5200, 5201) emphasizes the relative uniformity of composition of paragenetically identical monazites from the same pegmatite. In both cases the Σ's and the Ce/(Nd + Y) ratios (suggested by Murata *et al.*, 1957) are very close.

Paragenetically-identical monazites from different pegmatites in the same district (5185, 5186, 5187, 5188, 5197, 5189) (5195, 5196, 5202) (5191, 5193) also

show but minor rare-earth variations and a somewhat greater thorium variation, although by no means as large as between districts. Three distinct groupings of the monazites on the basis of their rare-earth distribution can be made: (a) the Petaca + the Pecos monazites (Σ = 66·3–69·9); (b) the Trout Creek Pass + the Baumer monazites (Σ = 66·1–67·1); and (c) the Brown Derby monazites (Σ = 51·4–55·6). It is noteworthy that the Elk Mountain pegmatites (Pecos monazite) are mineralogically and geologically similar to those of the Petaca

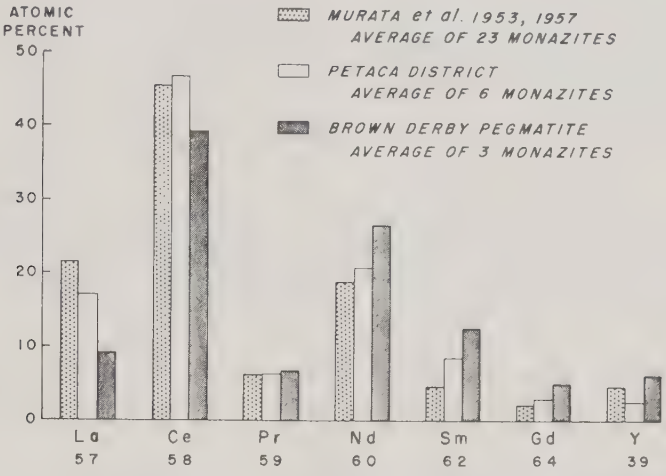

Fig. 1. Graphic presentation of rare-earth element distribution in selected monazites. (Numbers below chemical symbols are atomic numbers.)

district, and the two groups may be consanguineous. Likewise the Baumer pegamatite and those of Trout Creek Pass may well belong to the same pegmatite clan on the basis of mineralogy and geology. Thus, for the monazites here studied there appears to be a rare-earth element distribution that is characteristic for a particular pegmatite district. Fig. 1 presents a graphical comparison of the rare-earth distribution of monazites from the Brown Derby and Petaca districts, as well as an average of the twenty-three monazites analysed by Murata *et al.* (1953, 1957). To a somewhat lesser degree the Th content for a particular district appears restricted to a characteristic range. The data suggest that it may well be possible to correlate pegmatites on the basis of the rare-earth element distribution in their monazites.

The Brown Derby monazites are the only ones of the group not closely or commonly associated with a radioactive multiple-oxide mineral such as samarskite or euxenite; they also are very low in thorium. The Brown Derby monazites also are clearly magmatic in origin.* The Baumer monazites also are probably magmatic and are second lowest in thorium content. That any more general significance can be attached to this relationship seems unlikely inasmuch as

* For detailed presentations of the data on internal structures, mineral parageneses and conclusions on the origins of the monazites in the various districts, reference may be made to the literature for the various districts: Jahns (1946), Staatz and Trites (1955), Hanley *et al.* (1950), Heinrich and Bever (1957).

Murata *et al.* (1957, monazites 6 and 19) found less thorium in a pegmatitic monazite than in a monazite from the genetically related normal quartz monazite. Thorium variations appear to be relatable chiefly to district characteristics.

Distribution of Thorium

Autoradiographs were prepared of specimens from nearly all of the localities represented by the analysed monazites. The autoradiographs display three types of density patterns:

1. Essentially homogeneous distribution of the radioactive elements (North Star, Coats, Brown Derby no. 1 and no. 2, Yard, Luella).
2. Crystallographically oriented zones of contrasting radioactivity (Brown Derby no. 1, Fridlund).
3. Non-systematic variations in radioactivity (North Star, Pecos, Luella, Baumer).

Although the differences in intensity are slight, they are readily discernable on autoradiographs of 15 hr exposure. These autoradiographs also clearly reflected the differences in overall ThO_2 content revealed by the analyses: the autoradiographs of the Brown Derby specimens were by far the lightest.

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	U.S. Geol. Survey emission spectroscopy (wt. %)	This paper X-ray fluorescence (wt. %)
La_2O_3	24·9	25·5
CeO_2	48·2	49·6
Pr_6O_{11}	5·1	4·4
Nd_2O_3	16·8	16·3
Sm_2O_3	2·2	2·5
Gd_2O_3	0·6	0·3
Y_2O_3	1·8	1·5

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LETTER TO THE EDITOR

Comments on the recent letter on "Moldavites and similar tektites from Georgia, U.S.A."*

(*Received* 2 *January* 1960)

AUSTRALITES are said to be "apparently the most recent tektites, being found on the desert surface still containing delicate surface features absent in all other tektites". In actual fact, virtually all of the specimens of australites found in the arid portions of the strewnfield, and most of those from marginal areas of sub-arid character, have lost all or nearly all of their primary and secondary sculpture features and patterns from the action of relatively intensive subaerial erosion. This has led to the removal of original outer surface layers of the australites in varying amounts, so that the surficial features now exposed to view are merely an expression of the complex internal flow patterns in such of the worn specimens as have also been subjected to solution etching after abrasion. The majority of worn specimens, however, reveal no original "delicate surface features", and the shapes of many of the remnant forms are too indefinite to be classified with the established shape types of australites with any degree of certainty. Abrasion and solution etching, therefore, have removed and destroyed the unique circumferential flange structures and the flow ridges that are so characteristic of the anterior surfaces of better-preserved australites. They have also removed the primary bubble pits and flow-swirled structures from the posterior surfaces. In two collections of australites from the more arid regions, only one worn flange fragment detached from its parent form is recorded among approximately 11,000 specimens, and this number represents between one-third and one-quarter of the australites in known collections; moreover, none of the remnant body portions of the australites retain any traces of attached circumferential flange structures.

It is only in the more temperate regions within the australite strewnfield that the original primary and secondary surface features of australites are well preserved. Even in such areas, well-preserved australites only occur in restricted parts where they have remained buried and preserved under the right conditions in thin, superficial soil covers for most or all of the time that has elapsed since their fall to earth (approximately 5000 years). The most perfectly developed australites ever yet recovered from the whole of the Australian stewnfield come from the Port Campbell district on the southern coast of western Victoria, but even here, several specimens have been fragmented, others somewhat abraded when exposed, and some have been relatively deeply etched by soil solutions. The rainfall in this district has averaged 30 in. per annum over the past 50 years, and cannot therefore come into the category of having a "desert surface".

The further statement that australites "cover a large portion of the Australian continent" could convey an inaccurate concept of australite distribution, and might even indicate to the uninitiated that there was a relatively even spread of specimens over a very large area. The australite strewnfield occupies some 2,000,000 miles^2 (i.e. nearly two-thirds) of the island continent, but the known distribution within the strewnfield is variable and of unequal spread. The australites certainly do not cover the whole of this area, and in many districts it is impossible to find a single specimen in many square miles of territory. In fact, only some 40,000 specimens have been so far recovered from the 2,000,000 miles^2 strewnfield; this is approximately one specimen in some 500 square miles, but the distribution is uneven. In parts, there is a sporadic scatter, with only a few specimens occurring here and there over wide areas. Over even vaster

* *Geochim. et Cosmochim. Acta* **17**, 150–152.

areas within the strewnfield, no specimens at all, or at most one or two, have been recovered. Elsewhere, but in very limited areas in a small number of districts widely separated in the strewnfield, several hundred to one thousand or so specimens have been found in what may be regarded as concentration centres. In several such centres, concentration has been effected by streams that have washed and rolled australites into placer deposits. In very few of the centres (three or four) is the concentration probably due to a primary cause (i.e. extraterrestrial).

On page 150, Table 1, a specimen of a moldavite registered as No. 86240 in the U.S. Museum collection is listed as coming from the locality "Moldavia". Unfortunately this is an error that has all too often crept into tektite literature. No true tektites have as yet been authoritatively recorded from Moldavia which is a region on the north-western shores of the Black Sea, and some 600 to 700 miles east-southeast of the ancient kingdoms of Bohemia and Moravia. The tektites known as moldavites are found in Moravia and Bohemia, and are named after the place of their first discovery, near the township of Moldava on the Moldave river in Czechoslovakia.

George Baker

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Shunji Umemoto: An example of variations in constituents of hot springs

F. Fröhlich: Beitrag zur Geochemie des Chroms

S. Matthes: Ergebnisse zur Granatsynthese und ihre Beziehungen zur natürlichen Granatbildung innerhalt der Pyralspit-Gruppe

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